AD-A110 930 MESSINA UNIV (ITALY) DEPT OF PHYSICS F/G 20/6

THE OPTICAL SPECTRA OF MOLECULAR AEROSOLS.(U)

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THE OPTICAL SPECTRA OF MOLECULAR AEROSOLS

Final Technical Report

by

F. Borghese, P. Denti, G. Toscano and O.I. Sindoni

October 1981

United States Army
EUROPEAN RESEARCH OFFICE OF THE U. S. ARMY
London England

Contract number DA ERO 78-G-106

Contractor: Prof. F. Borghese

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R&D 2598-EN

SECURITY CLASSIFICATION OF THIS PAGE (When Data Entered)

REPORT DOCUMENTATION PAGE		READ INSTRUCTIONS BEFORE COMPLETING FORM
1. REPORT NUMBER	2. GOVT ACCESSION NO. AD-A110 930	3. RECIPIENT'S CATALOG NUMBER
4. TITLE (and Subtitle) The Optical Spectra of Molecular Aerosols		5. TYPE OF REPORT & PERIOD COVERED Final Technical Report Sept. 78 - Oct 81
		6. PERFORMING ORG. REPORT NUMBER
7. AUTHOR(s) F. Borghese, P. Denti, G. Toscano, and O. I. Sindoni		8. CONTRACT OR GRANT NUMBER(s) DAERO-78-G-106
9. PERFORMING ORGANIZATION NAME AND ADDRESS Department of Physics University of Messina Messina, Italy		10. PROGRAM ELEMENT, PROJECT, TASK AREA & WORK UNIT NUMBERS 6.11.02A IT161102BH57-01
11. CONTROLLING OFFICE NAME AND ADDRESS USARDSG-UK Box 65, FPO NY 09510		12. REPORT DATE October 1981
		13. NUMBER OF PAGES 54
14. MONITORING AGENCY NAME & ADDRESS (if different from Controlling Office)		15. SECURITY CLASS. (of this report) Unclassified
		15a. DECLASSIFICATION/DOWNGRADING SCHEDULE

16. DISTRIBUTION STATEMENT (of this Report)

Approved for public release; Distribution unlimited

17. DISTRIBUTION STATEMENT (of the abstract entered in Block 20, if different from Report)

18. SUPPLEMENTARY NOTES

19. KEY WORDS (Continue on reverse side if necessary and identify by block number)

Aerosols; Optical spectra; electromagnetic radiation; optical scattering; multiple scattering; refractive index; optical transmission

20. ABSTRACT (Continue on reverse side if necessary and identify by block number)

A method to calculate the electromagnetic scattering properties of a cluster of spheres of arbitrary radia and (possibly complex) refractive indexes is proposed. The approach takes proper account of multiple scattering effects through an appropriate addition theorem for Vector Helmholtz Harmonics which is preliminary formulated. No approximation is required but the truncation of the multipolar expansion of the scattered field. Group theory is also used to factorize the resulting system

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S/N 0102-LF-014-6601

Unclassified

SECURITY CLASSIFICATION OF THIS PAGE (When Data Entered)

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of linear nonhomogeneous equations.

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Summary.

A method to calculate the electromagnetic scattering properties of a cluster of spheres of arbitrary radia and (possibly complex) refractive indexes is proposed. The approach takes proper account of multiple scattering effects through an appropriate addition theorem for Vector Helmholtz Harmonics which is preliminarly formulated. No approximation is required but for the truncation of the multipolar expansion of the scattered field. Group theory is also used to factorize the resulting system of linear nonhomogeneous equations.

1. Introduction.

As is well known, the problem of the electromagnetic scattering from irregularly shaped objects has not been soved in general but from a conceptual point of view[1,2]. For this reason this paper dels only with the scattering from spherical objects or from objects composed of spherical, though not necessarily homogeneous scatterers. We shall, in fact, introduce a model scatterer composed by a cluster of spheres whose relative positions, radia and (possibly complex) refractive indexes are assumed to be known. We are able to describe the field scattered by such an object in a rather simple way and to take account of multiple scattering among the spheres in the cluster. It will become apparent that such a model scatterer should be suitable to approximate the scattering properties of molecules, even the most asymmetrical ones.

In the course of our description we will make large use of the vector solutions of Helmholtz equation in spherical coordinates. Although these functions are thoroughly described in the literature, the material is rather scattered. Therefore, in the first few paragraphs, we summarize the main properties of these functions. Of course our description does not pretend to be complete, for it will be restricted to the topics of interest for our purposes. Further, we shall give a detailed description of our model scatterer and discuss the technique to calculate the scattered field and related quantities.

2. The field equations.

Any theory of the electromagnetic scattering should start from Maxwell equations for stationary media, which we shall rewrite here in gaussian units[3,4]

$$\nabla \times \underset{\sim}{H} = \frac{4\pi}{c}\underset{\sim}{j} + \frac{1}{c}\frac{\partial \underset{\sim}{D}}{\partial t} \qquad (2\text{-}1a)$$

$$\nabla \times \underset{\sim}{E} = -\frac{1}{c}\frac{\partial \underset{\sim}{B}}{\partial t} \qquad (2\text{-}1b)$$

$$\nabla \cdot \underset{\sim}{D} = 4\pi\rho \qquad (2\text{-}1c)$$

$$\nabla \cdot \underset{\sim}{B} = 0 \qquad (2\text{-}1d)$$

together with the constitutive equations of the medium

$$\underset{\sim}{D} = \varepsilon \underset{\sim}{E} \qquad (2\text{-}2a)$$

$$\underset{\sim}{B} = \mu \underset{\sim}{H} \qquad (2\text{-}2b)$$

$$\underset{\sim}{j} = \sigma \underset{\sim}{E} \qquad (2\text{-}2c)$$

In the following we shall deal with nonmagnetic ($\mu \approx 1$) and isotropic media and assume an harmonic time dependence of all fields so that, e.g.

$$\underset{\sim}{E}(\underset{\sim}{r},t) = \underset{\sim}{E}(\underset{\sim}{r})\exp(-i\omega t) \qquad (2\text{-}3)$$

With these assumptions, equations (2-1a) and (2-1b) read

$$\nabla \times \underset{\sim}{B} = -ikn^2\underset{\sim}{E} \qquad (2\text{-}4a)$$

$$\nabla \times \underset{\sim}{E} = ik\underset{\sim}{B} \qquad (2\text{-}4b)$$

where $k=\omega/c$ is the magnitude of the propagation vector and

$$n^2 = \mu\left[\varepsilon + \frac{4\pi i\sigma}{\omega}\right] \qquad (2\text{-}5)$$

is the complex refractive index. Furthermore, eq. (2-1c) becomes

$$\nabla \cdot n^2 \underset{\sim}{E} = 0 \ . \qquad (2\text{-}6)$$

Although we did not assume that the medium be homogeneous, so that both ε and σ can depend on the coordinates, we need not bother with thir frequency-dependence thanks to the assumption of harmonic time-dependence, eq.(2-3), provided that the values of ε and σ be those appropriate to the frequency at hand.

It is now a simple matter to show that E and B are the solutions of the equations

$$\nabla\times\nabla\times \underset{\sim}{E} - k^2 n^2 \underset{\sim}{E} = 0 \qquad (2\text{-}7a)$$

$$\nabla\times\nabla\times \underset{\sim}{B} - k^2 n^2 \underset{\sim}{B} = -ik \, \nabla n^2 \times \underset{\sim}{E} \qquad (2\text{-}7b)$$

which are not decoupled on account of the assumed non-homogeneity of the medium.

3. The vector Helmholtz equation and its solutions.

In order to discuss the structure of the solutions of equations (2-7) let us consider first a homogeneous medium. The above equations then become

$$(\nabla^2 + K^2)\underset{\sim}{E} = 0 \qquad (3\text{-}1a)$$

$$(\nabla^2 + K^2)\underset{\sim}{B} = 0 \qquad (3\text{-}1b)$$

with K = kn, i.e. both E and B should satisfy a vector Helmholtz equation. This statement means that each of the components of E and B is the solution of a corresponding scalar Helmholtz equation. However this is in no way true in any other system of coordinates: even in orthogonal coordinates it is impossible to separate eqs. (3-1) into three scalar equations each involving only one component of the field[5]. It si therefore convenient to search for general vector solutions of the Helmholtz equation

a. Hansen's vectors.

Let us consider the scalar Helmholtz equation

$$(\nabla^2 + K^2)\,\psi = 0 \qquad (3\text{-}2)$$

and let $\hat{O}$ be a vector operator capable of acting on its solutions, ψ. Then we have

$$\hat{\underset{\sim}{O}}(\nabla^2 + K^2)\,\psi = (\nabla^2 + K^2)\hat{\underset{\sim}{O}}\,\psi + [\hat{\underset{\sim}{O}}, \nabla^2]\,\psi \qquad (3\text{-}3)$$

i.e. for any vector operator such that $[\hat{\underset{\sim}{O}}, \nabla^2] = 0$, $\hat{\underset{\sim}{O}}\,\psi$ is a vector solution of Helmholtz equation[6]. Now two operators with this property are the gradient operator, ∇, which is proportional to the linear momentum operator, $\mathrm{P} = -i\nabla$, and the angular momentum operator $\hat{\underline{L}} = -i\underset{\sim}{r} \times \nabla$. We have then to search for a third operator for, on general mathematical grounds, Helmholtz equation should have three linearly independent vector solutions for each value of K. To this end let us recall that if A is a vector solution, also $\nabla \times \underline{A}$ is. Thus the only other independent solu-

tion is $\nabla\times\nabla\times\underline{A}$. Ultimately, given any scalar solution of Helmholtz equation, the three vector functions[5,7]

$$\underline{L} = \nabla\psi \quad , \quad \underset{\sim}{M} = \hat{\underline{L}}\,\psi \quad , \quad \underset{\sim}{N} = \frac{1}{K}\,\nabla\times\hat{\underline{L}}\,\psi \qquad (3\text{-}4)$$

known in the literature as Hansen's vectors form a complete set of vector solutions. The factor 1/K in the definition of $\underline{N}$ has been introduced so that

$$\nabla\times\underset{\sim}{M} = \underset{\sim}{N} \qquad (3\text{-}5)$$

b. Irreducible spherical tensors.

Hansen's vectors are defined in any system of coordinates and are therefore quite general. They do not form, however, an ortogonal set for

$$\underline{L}\cdot\underset{\sim}{M} = 0 \quad , \quad \underset{\sim}{M}\cdot\underset{\sim}{N} = 0$$

but

$$\underset{\sim}{L}\cdot\underset{\sim}{N} \neq 0$$

and this may be trublesome in several applications. We shall therefore introduce a new independent set of solutions which, although defined only in spherical coordinates, form a complete orthogonal set and have very useful mathematical properties. To this end let us search for the transformation properties of a vector field, $\underline{F}(x,y,z)$, under infinitesimal rotations of the coordinate axes. As is well known, the infinitesimal rotation operator is[8]

$$\mathcal{R}(d\underset{\sim}{\omega}) = (1 + i\, d\underset{\sim}{\omega}\cdot\hat{\underset{\sim}{J}})$$

where $\hat{\underline{J}}$ is the angular momentum operator, so that

$$\underset{\sim}{F}'(x',y',z') = (1 + i\, d\underset{\sim}{\omega}\cdot\hat{\underset{\sim}{J}})\,\underset{\sim}{F}(x,y,z) \qquad (3\text{-}6)$$

Now, by working the transformation of the rectangular components of $\underline{F}$ and comparing with eq. (3-6), one easily sees that

$$\hat{\underset{\sim}{J}} = \hat{\underset{\sim}{L}} + \hat{\underset{\sim}{S}} = -i\,\underset{\sim}{r} \times \nabla + \hat{\underset{\sim}{S}}$$

where $\underline{S}$ is a set of three 3×3 matrices which represent the intrinsic spin of the vector field[9]. The simultaneous eigenvectors of $\hat{S}^2$ and $\hat{S}_z$ can be shown to be

$$\underset{\sim}{\xi}_{\pm 1} = \mp \frac{1}{\sqrt{2}}(\underset{\sim}{e}_x \pm i\underset{\sim}{e}_y) \quad , \quad \underset{\sim}{\xi}_0 = \underset{\sim}{e}_z \tag{3-7}$$

where $\underline{e}_x$, $\underline{e}_y$ and $\underline{e}_z$ are unit vectors along the x, y and z axes, respectively. It is apparent from the above equations that the intrinsic spin of any vector field is 1. As the simultaneous eigenvectors of L^2 and L_z in spherical coordinates are the well known spherical harmonics, Y_{LM}, we can couple the Y's and the $\underset{\sim}{\xi}$'s by means of the vector coupling coefficients and get the simultaneous eigenvectors of J^2, J_z, L^2 and S^2 :

$$\underset{\sim}{T}^M_{JL}(\hat{\underset{\sim}{r}}) = \sum_{\mu} C(1,L,J;-\mu,M+\mu)\,Y_{L\,M+\mu}(\hat{\underset{\sim}{r}})\,\underset{\sim}{\xi}_{-\mu} \tag{3-8}$$

The vectors $\underline{T}^M_{JL}(\hat{\underline{r}})$ are the components of an irreducible spherical tensor pf rank 2J+1 and, under rotation of the coordinate axes transform according to[10]

$$\underset{\sim}{T}'^{M}_{JL}(\hat{\underset{\sim}{r}}') = \sum_{M'} \mathcal{D}^{(J)}_{M'M}\,\underset{\sim}{T}^{M'}_{JL}(\hat{\underset{\sim}{r}}), \tag{3-9}$$

while their parity is $(-)^L$. The triangular condition on the Clebsch-Gordan coefficients, $\Delta(1,L,J)$, imposes that

for each value of J there exist only three mutually orthogonal tensors, $\underset{\sim}{T}^{M}_{LL}$, $\underset{\sim}{T}^{M}_{LL\pm1}$. Now it is of immediate verification that the vector functions

$$\underset{\sim}{A}^{M}_{JL}(\underset{\sim}{r}) = f_L(kr)\,\underset{\sim}{T}^{M}_{JL}(\hat{\underset{\sim}{r}}) \qquad (3\text{-}10)$$

where f_L is a spherical Bessel, Neumann or Hankel function, are solutions of the Helmholtz equation in spherical coordinates. They will be referred to in the following as Vector Helmholtz Harmonics (VHH).

c. Vector Spherical Harmonics (VSH).

When one has to impose to the electromagnetic field the customary boundary conditions at the surface of a sphere, the VHH's are not the most useful set of basis functions for $\underset{\sim}{T}^{M}_{LL\pm1}$ are neither tangent nor orthogonal to the surface, whereas $\underset{\sim}{T}^{M}_{LL}$ is. We can, however, take linear combinations of $\underset{\sim}{T}^{M}_{LL\pm1}$ which do are orthogonal and tangent to the surface of the unit sphere. Therefore we define

$$\underset{\sim}{X}_{LM}(\hat{\underset{\sim}{r}}) = -\,\underset{\sim}{T}^{M}_{LL}(\hat{\underset{\sim}{r}}) \qquad (3\text{-}11a)$$

$$\hat{\underset{\sim}{r}}\,Y_{LM}(\hat{\underset{\sim}{r}}) = -\sqrt{\frac{L+1}{2L+1}}\,\underset{\sim}{T}^{M}_{LL+1} + \sqrt{\frac{L}{2L+1}}\,\underset{\sim}{T}^{M}_{LL-1} \qquad (3\text{-}11b)$$

$$\hat{\underset{\sim}{r}}\times\underset{\sim}{X}_{LM}(\hat{\underset{\sim}{r}}) = \sqrt{\frac{L}{2L+1}}\,\underset{\sim}{T}^{M}_{LL+1} + \sqrt{\frac{L+1}{2L+1}}\,\underset{\sim}{T}^{M}_{LL-1} \qquad (3\text{-}11c)$$

The above functions, known in the literature as Vector Spherical Harmonics, are orthogonal to each other and,

when multiplied by $f_L(kr)$, form a complete set of solutions of the vector Helmholtz equation. Thir relation to Hansen's $\underline{M}$ and $\underline{N}$ vectors in spherical coordinates is given by the equations

$$\underset{\sim}{M}_{LM}(\underset{\sim}{r}) = f_L(kr)\underset{\sim}{X}_{LM}(\hat{\underset{\sim}{r}}), \quad \underset{\sim}{N}_{LM}(\underset{\sim}{r}) = \frac{1}{k}\nabla\times f_L(kr)\underset{\sim}{X}_{LM}(\hat{\underset{\sim}{r}}).$$

We notice that the solenoidal character of $\underline{M}_{LM}$ and of $\underline{N}_{LM}$, which is quite evident from the above equations, allows to expand any solenoidal field, such as $n^2\underline{E}$ and $\underline{B}$, in their terms only. In this case $\underline{M}_{LM}$, of parity $(-)^L$, is said to represent a magnetic multipole of order 2^L, while $\underline{N}_{LM}$, of parity $(-)^{L+1}$, represents an electric multipole of the same order. The relation between Hansen's $\underline{L}$ vector and the VSH's is rather complicated and will, however, never be used in our work.

4. An addition theorem for VHH's.

a. The addition theorem.

In the course of our work we shall need to relate to each other the VHH's centered at the eigin of two mutually translated systems of spherical coordinates. To do this we start from the addition theorem for scalar Helmholtz harmonics wchich we rewrite here in a form slightly different from that reported by Nozawa[12]:

$$f_L(kr)Y_{LM}(\hat{\underset{\sim}{r}}) = \sum_{L'M'} G_{L'M'LM}(-\underset{\sim}{R})\, g_{L'}(kr')\, Y_{L'M'}(\hat{\underset{\sim}{r}}') \qquad (4.1)$$

where the quantities

$$G_{L'M'LM}(\underset{\sim}{R}) = 4\pi \sum_{\lambda} i^{L'-L-\lambda} I_\lambda(L'M';LM)\ \psi_\lambda(kR)\, Y^{*}_{\lambda M'-M}(\hat{\underset{\sim}{R}}) \qquad (4\text{-}2)$$

with $\underline{r}' = \underline{r} - \underline{R}$, are the matrix elements, in the angular momentum representation of the free space propagator for spherical waves. In eq. (4-1) and (4-2) when $f_L = j_L$, $\psi_\lambda = j_\lambda$ and $g_{L'} = j_{L'}$, but when $f_L = h_L$

$$\psi_\lambda = h_\lambda\ ,\ g_{L'} = j_{L'} \quad : \ r' < R$$

$$\psi_\lambda = j_\lambda\ ,\ g_{L'} = h_{L'} \quad : \ r' > R$$

and the quantities

$$I_\lambda(L'M';LM) = \int Y^{*}_{L'M'}\, Y_{LM}\, Y_{\lambda M'-M}\ d\Omega \qquad (4\text{-}3)$$

are the well known Gaunt integrals[13]. Now we recall that a VHH is defined as

$$\underset{\sim}{A}{}^{M}_{JL}(\underset{\sim}{r}) = f_L(kr)\, \underset{\sim}{T}{}^{M}_{JL}(\hat{\underset{\sim}{r}}) =$$

$$= \sum_{\mu} C(1,L,J;-\mu,M+\mu)\, f_L(kr)\, Y_{LM+\mu}(\hat{\underset{\sim}{r}})\, \underset{\sim}{\xi}_{-\mu} \qquad (4\text{-}4)$$

so that we can substitute eq. (4-1)into eq. (4-4) to get

$$\underset{\sim}{A}{}^{M}_{JL}(\hat{\underset{\sim}{r}}) = \sum_{\mu} C(1,L,J;-\mu,M+\mu) \sum_{L'M''} G_{L'M''LM+\mu}(-\underset{\sim}{R}) \cdot$$

$$g_{L'}(kr')\, Y_{L'M''}(\hat{\underset{\sim}{r}}')\, \underset{\sim}{\xi}_{-\mu}$$

which can be written as

$$\underset{\sim}{A}^{M}_{JL}(\underset{\sim}{r}) = \sum_{\mu} C(1,L,J;-\mu,M+\mu) \sum_{L'M''} G_{L'M''LM+\mu}(-\underset{\sim}{R}) \cdot$$

$$\sum_{J'} C(1,L',J';-\mu,M'')\; g_{L'}(kr')\, \underset{\sim}{T}^{M''-\mu}_{J'L'}(\hat{\underset{\sim}{r}}')$$

through the use of the inverse to eq. (3-8). If we now put $M' = M'' - \mu$ and

$$\mathcal{G}^{M'M}_{J'L'JL} = \sum_{\mu} C(1,L'J';-\mu,M'+\mu)\, G_{L'M'+\mu LM+\mu}(-\underset{\sim}{R})\, C(1,L,J;-\mu,M+\mu)$$

we get

$$\underset{\sim}{A}^{M}_{JL}(\hat{\underset{\sim}{r}}) = \sum_{L'} \sum_{J'M'} \mathcal{G}^{M'M}_{J'L'JL}\; g_{L'}(kr')\, \underset{\sim}{T}^{M'}_{J'L'}(\hat{\underset{\sim}{r}}') \qquad (4\text{-}5)$$

which is the required addition theorem[14].

Equation (4-5) can be specialized to Hansen's $\underline{M}$ and $\underline{N}$ vectors through the use of the relations[11]

$$\underset{\sim}{M}_{LM} = f_L(kr)\, \underset{\sim}{X}_{LM}(\hat{\underset{\sim}{r}}) = -f_L(kr)\, \underset{\sim}{T}^{M}_{LL}(\hat{\underset{\sim}{r}})$$

$$\underset{\sim}{N}_{LM} = \frac{1}{k} \nabla \times \underset{\sim}{M}_{LM} = i\left[\sqrt{\frac{L+1}{2L+1}}\, f_{L-1}\, \underset{\sim}{T}^{M}_{LL-1} - \sqrt{\frac{L}{2L+1}}\, f_{L+1}\, \underset{\sim}{T}^{M}_{LL+1}\right].$$

Indeed we have for $\underline{M}_{LM}$:

$$\underset{\sim}{M}_{LM}(\underset{\sim}{r}) = -\sum_{L'M'} \Big\{ \mathcal{G}^{M'M}_{L'L'LL}\; g_{L'}(kr')\, \underset{\sim}{T}^{M'}_{L'L'}(\hat{\underset{\sim}{r}}') +$$

$$\mathcal{G}^{M'M}_{L'L'-1LL}\; g_{L'-1}(kr')\, \underset{\sim}{T}^{M'}_{L'L'-1}(\hat{\underset{\sim}{r}}') + \mathcal{G}^{M'M}_{L'L'+1LL}\; g_{L'+1}(kr')\, \underset{\sim}{T}^{M'}_{L'L'+1}(\hat{\underset{\sim}{r}}') \Big\}$$

$$(4\text{-}6)$$

whence, on account of the divergenceless character of $\underline{M}_{LM}$ the recursion relation follows

$$\sqrt{\frac{l'+1}{2l'+1}}\, \mathcal{G}^{M'M}_{l'l'+1,LL} + \sqrt{\frac{l'}{2l'+1}}\, \mathcal{G}_{l'l'-1,LL} \qquad (4\text{-}7)$$

which can also be proved by direct calculation making use of the recursion properties of the Clebsch-Gordan coefficients. With the help of equation (4-7), eq. (4-6) can be put into the form[15)]

$$\underset{\sim}{M}_{LM}(\underset{\sim}{r}) = \sum_{l'M'} \left[\mathcal{A}_{l'M'LM}\, \tilde{\underset{\sim}{M}}_{l'M'}(\underset{\sim}{r}') + \mathcal{B}_{l'M'LM}\, \tilde{\underset{\sim}{N}}_{l'M'}(\underset{\sim}{r}') \right] \qquad (4\text{-}8)$$

where we put

$$\mathcal{A}_{l'M'LM} = \mathcal{G}^{M'M}_{l'l',LL} \quad , \quad \mathcal{B}_{l'M'LM} = -i\sqrt{\frac{2l'+1}{l'}}\, \mathcal{G}^{M'M}_{l'l'+1,LL} \qquad (4\text{-}9)$$

The functions $\tilde{\underline{M}}$ and $\tilde{\underline{N}}$ are identical to $\underline{M}$ and $\underline{N}$, respectively, but for the substitution of g_L to f_L. In the following the quantities $\mathcal{A}$ and $\mathcal{B}$ will be indicated by $\mathcal{H}_{l'M'LM}$ and $\mathcal{K}_{l'M'LM}$, respectively, when $\mathcal{G}$ contains h_λ and by $\mathcal{J}_{l'M'LM}$ and $\mathcal{L}_{l'M'LM}$, respectively when $\mathcal{G}$ contains j_λ.

b. Matrix elements of the dyadic Green function.

In this section we will show that the quantities are the matriw elements of the dyadic Green function for free space propagation of spherical vector waves. To this end we recall that this fuction is the solution of the inhomogeneous vector Helmholtz equation

$$(\nabla^2 + k^2)\underset{\sim}{G}(\underset{\sim}{r},\underset{\sim}{r}') = -4\pi\, \mathbb{1}\, \delta(\underset{\sim}{r}-\underset{\sim}{r}') \,,$$

and has the form

$$\underset{\sim}{G}(\underset{\sim}{r},\underset{\sim}{r}') = \mathbb{1}\,\frac{e^{ik|\underset{\sim}{r}-\underset{\sim}{r}'|}}{|\underset{\sim}{r}-\underset{\sim}{r}'|} \qquad (4\text{-}10)$$

where $\mathbb{1}$ is the unit dyadic. If, for greater generality we consider two points in space at $\underset{\sim}{R}_\alpha$ and $\underset{\sim}{R}_\beta$ and put $\underset{\sim}{r}_\alpha = \underset{\sim}{r} - \underset{\sim}{R}_\alpha$, $r'_\beta = \underset{\sim}{r}' - \underset{\sim}{R}_\beta$, eq. (4-10) can be rewritten as

$$\underset{\sim}{G}(\underset{\sim}{r}_\alpha,\underset{\sim}{r}'_\beta) = \mathbb{1}\,\frac{e^{ik|\underset{\sim}{r}_\alpha - \underset{\sim}{r}'_\beta - \underset{\sim}{R}_{\alpha\beta}|}}{|\underset{\sim}{r}_\alpha - r'_\beta - \underset{\sim}{R}_{\alpha\beta}|} \qquad (4\text{-}11)$$

with $\underset{\sim}{R}_{\alpha\beta} = \underset{\sim}{R}_\beta - \underset{\sim}{R}_\alpha$. Neuman expansion of eq. (4-11) is

$$\underset{\sim}{G}(\underset{\sim}{r}_\alpha,\underset{\sim}{r}'_\beta) = 4\pi i k\,\mathbb{1}\sum_{LM} h_L(k|\underset{\sim}{r}_\alpha - \underset{\sim}{R}_{\alpha\beta}|)\,Y_{LM}(\underset{\sim}{r}_\alpha - \underset{\sim}{R}_{\alpha\beta})\,j_L(kr'_\beta)\,Y^*_{LM}(\underset{\sim}{r}'_\beta)$$

on the assumption that $|\underset{\sim}{r}_\alpha - \underset{\sim}{R}_{\alpha\beta}| \geq r'_\beta$. By assuming further that $r_\alpha < \underset{\sim}{R}_{\alpha\beta}$ the addition theorem of eq.(4-1) can be applied to $h_L(k|\underset{\sim}{r}_\alpha - \underset{\sim}{R}_{\alpha\beta}|)\,Y_{LM}(\underset{\sim}{r}_\alpha - \underset{\sim}{R}_{\alpha\beta})$:

$$\underset{\sim}{G}(\underset{\sim}{r}_\alpha,\underset{\sim}{r}'_\beta) = 4\pi i k \sum_\mu \sum_{LM}\sum_{L'M'} j_L(kr'_\beta)\,Y^*_{LM}(\underset{\sim}{r}'_\beta)\,\underset{\sim}{\xi}^*_{-\mu}\,G_{L'M'LM}(\underset{\sim}{R}_{\alpha\beta})\,j_{L'}(kr_\alpha)\,Y_{L'M'}(\hat{\underset{\sim}{r}}_\alpha)\,\underset{\sim}{\xi}_{-\mu} \qquad (4\text{-}12)$$

where we expanded the unit dyadic in a spherical basis:

$$\mathbb{1} = \sum_\mu (-)^\mu\,\underset{\sim}{\xi}_\mu\,\underset{\sim}{\xi}_{-\mu} = \sum_\mu \underset{\sim}{\xi}^*_{-\mu}\,\underset{\sim}{\xi}_{-\mu}$$

Now we recall that the spherical harmonics and the irreducible spherical tensors are related through the equation

$$\underset{\sim}{\xi}_{-\mu}\,Y_{LM}(\hat{\underset{\sim}{r}}) = \sum_J C(1,L,J;-\mu,M)\,\underset{\sim}{T}^{M-\mu}_{JL}(\hat{\underset{\sim}{r}})$$

so that eq. (4-12) can be rwritten as

$$\underset{\sim}{G}(r_\alpha,r'_\beta) = 4\pi i k \sum_\mu \sum_{JJ'}\sum_{LM}\sum_{L'M'} j_L(kr'_\beta)\,\underset{\sim}{T}^{M-\mu\,*}_{JL}(\hat{\underset{\sim}{r}}'_\beta)\,C(1,L,J;-\mu,M).$$

$$G_{L'M'LM}(\underset{\sim}{R}_{\alpha\beta})\, C(1,L',J';-\mu,M')\, j_{L'}(kr_\alpha)\, \underset{\sim}{T}_{J'L'}^{M'-\mu}(\hat{\underset{\sim}{r}}_\alpha)$$

which, through the position $M-\mu=m$, $M'-\mu=m'$, takes the final form

$$\underset{\sim}{G}(\underset{\sim}{r}_\alpha,\underset{\sim}{r}_\beta)=\sum_{JM}\sum_{J'M'}\sum_{LL'} j_L(kr'_\beta)\,\underset{\sim}{T}_{JL}^{m*}(\hat{\underset{\sim}{r}}'_\beta)\, \mathcal{G}_{J'L'JL}^{m'm}(\underset{\sim}{R}_{\alpha\beta})\, j_{L'}(kr_\alpha)\,\underset{\sim}{T}_{J'L'}^{M'}(\hat{\underset{\sim}{r}}_\alpha). \tag{4-13}$$

Eq. (4-13) shows that the quantities

$$\mathcal{G}_{J'L'JL}^{m'm}(\underset{\sim}{R}_{\alpha\beta})=\sum_\mu C(1,L,J;-\mu,m+\mu)\,G_{L'M'+\mu LM+\mu}(\underset{\sim}{R}_{\alpha\beta})\,C(1,L',J';-\mu,m'+\mu) \tag{4-14}$$

are just the matrix elements of $\underset{\sim}{G}$ with respect to VHH's centered at different sites of space.

We want to remark that the same result would be obtained if we assumed $|\underset{\sim}{r}_\alpha-\underset{\sim}{R}_{\alpha\beta}|\leq r'_\beta$ and/or $r_\alpha>R_{\alpha\beta}$, but for that the VHH's centered at $\underset{\sim}{R}_\alpha$ would contain h_L instead of j_L and $G_{L'M'LM}$ would contain j_λ instead of h_λ. Finally we notice that the quantitiesdefined in eq. (4-14) are the off diagonal(in the site indexes) elements of $\underset{\sim}{G}$, whereas the quantities defined in eq. (4-5) are the corresponding on diagonal elements.

5. Scattering from a radially symmetric sphere.

The theory of electromagnetic scattering from a homogeneous sphere is well known since the work of Mie[17]. In this section we will study the scattering

from a radially symmetric sphere, i.e. with $n=n(r)$, of radius b, with the twofold purpose of finding the general expression of $\underline{E}$ and $\underline{B}$ within an inhomogeneous medium and of defining several quantities which will be useful for subsequent work.

a. The electromagnetic field within a radially symmetric sphere[18].

As shown in section 2 the $\underline{E}$ and $\underline{B}$ fields within a nonhomogeneous medium should satisfy eqs. (2-7). However in such a medium $\nabla\cdot\underset{\sim}{E}\neq 0$ so that eq. (2-7a) cannot be cast in Helmholtz form. It is therefore more convenient to search for solutions of the Maxwell equations. To this end we expand $\underline{E}$ and $\underline{B}$ in a series of VSH's

$$\underset{\sim}{E}=\sum_{LM}\left[C_{LM}R_L(r)\underset{\sim}{X}_{LM}(\hat{r})+\frac{1}{n^2}D_{LM}\frac{1}{k}\nabla\times S_L(r)\underset{\sim}{X}_{LM}(\hat{r})\right] \qquad (5\text{-}1a)$$

$$\underset{\sim}{B}=\sum_{LM}\left[D_{LM}S_L(r)\underset{\sim}{X}_{LM}(\hat{r})+C_{LM}\frac{1}{k}\nabla\times R_L(r)\underset{\sim}{X}_{LM}(\hat{r})\right] \qquad (5\text{-}1b)$$

which satisfy eqs. (2-6) and (2-1d), respectively, for any choice of the radial functions R_L and S_L. These latter are determined by substitution of eqs. (5-1) into the Maxwell equations (2-4). Indeed, it is easily seen that the radial functions should be the solutions, regular at r=0, of the equations

$$\left[\frac{d^2}{dr^2}-\frac{L(L+1)}{r^2}+k^2n^2\right](rR_L(r))=0 \qquad (5\text{-}2a)$$

$$\left[\frac{d^2}{dr^2}-\frac{L(L+1)}{r^2}-\frac{2}{rn}\frac{dn}{dr}\frac{d}{dr}+k^2n^2\right](rS_L(r))=0, \qquad (5\text{-}2b)$$

respectively. The expansion coefficients C_{LM} and D_{LM} are then determined by the requirement that $\underline{E}$ and $\underline{B}$ undergo the appropriate boundary conditions at the surface of the medium.

b. The incident plane wave.

We assume that the field inciding on the sphere has the form of a circularly polarized plane wave of wavevector $\underline{k}$:

$$\underset{\sim}{E}_\eta = (\underset{\sim}{e}_1 + i\eta \underset{\sim}{e}_2)\, e^{i\underset{\sim}{k}\cdot\underset{\sim}{r}} \tag{5-3a}$$

$$i\underset{\sim}{B}_\eta = \eta(\underset{\sim}{e}_1 + i\eta \underset{\sim}{e}_2)\, e^{i\underset{\sim}{k}\cdot\underset{\sim}{r}} \tag{5-3b}$$

where $\underline{e}_1$ and $\underline{e}_2$ are unit vectors orthogonal to $\underline{k}$ and to each other and $\eta = \pm 1$ according to the polarization. The direction of the propagation vector, $\underline{k}$, is assumed to be quite general. Now, if we assume for $\underline{E}_\eta$ and $\underline{B}_\eta$ the expansions in VSH's

$$\underset{\sim}{E}_\eta = \sum_{LM}\left[a_{\eta LM}\, j_L(kr)\underset{\sim}{X}_{LM}(\hat{\underset{\sim}{r}}) + b_{\eta LM}\frac{i}{k}\nabla\times j_L(kr)\underset{\sim}{X}_{LM}(\hat{\underset{\sim}{r}})\right]$$

$$i\,\underset{\sim}{B}_\eta = \sum_{LM}\left[b_{\eta LM}\, j_L(kr)\underset{\sim}{X}_{LM}(\hat{\underset{\sim}{r}}) + a_{\eta LM}\frac{i}{k}\nabla\times j_L(kr)\underset{\sim}{X}_{LM}(\hat{\underset{\sim}{r}})\right]$$

a straightforward but lenghty calculation shows that[3)]

$$a_{\eta LM} = 4\pi\, i^L (\underset{\sim}{e}_1 + i\eta\underset{\sim}{e}_2)\cdot \underset{\sim}{X}^{*}_{LM}(\hat{\underset{\sim}{k}})$$

$$i\, b_{\eta LM} = \eta\, a_{\eta LM}$$

Thus the expansion of the incident wave in VSH's is

$$\underset{\sim}{E}_\eta = \sum_{LM} W_{\eta LM}(\hat{\underset{\sim}{k}})\left[j_L(kr)\underset{\sim}{X}_{LM}(\hat{\underset{\sim}{r}}) + \eta\frac{1}{k}\nabla\times j_L(kr)\underset{\sim}{X}_{LM}(\hat{\underset{\sim}{r}})\right] \tag{5-4a}$$

$$i\underset{\sim}{B}_\eta = \sum_{LM} \eta\, W_{\eta LM}(\hat{\underset{\sim}{k}})\left[j_L(kr)\underset{\sim}{X}_{LM}(\hat{\underset{\sim}{r}}) + \eta\frac{1}{k}\nabla\times j_L(kr)\underset{\sim}{X}_{LM}(\hat{\underset{\sim}{r}})\right] \quad (5\text{-}4b)$$

where

$$W_{\eta LM}(\hat{\underset{\sim}{k}}) = 4\pi i^L(\underset{\sim}{e}_1 + i\eta\underset{\sim}{e}_2)\cdot\underset{\sim}{X}^*_{LM}(\hat{\underset{\sim}{k}}) \quad (5\text{-}5)$$

contains the dependence on the direction of $\underset{\sim}{k}$.

c. The scattered field.

The only ingredient we need to solve our scattering problem is the scattered field which we assume in the form

$$\underset{\sim}{E}^{(1)}_\eta = \sum_{LM}\left[A_{\eta LM}\, h_L(kr)\underset{\sim}{X}_{LM}(\hat{\underset{\sim}{r}}) + B_{\eta LM}\frac{1}{k}\nabla\times h_L(kr)\underset{\sim}{X}_{LM}(\hat{\underset{\sim}{r}})\right] \quad (5\text{-}6a)$$

$$i\underset{\sim}{B}^{(1)}_\eta = \sum_{LM}\left[B_{\eta LM}\, h_L(kr)\underset{\sim}{X}_{LM}(\hat{\underset{\sim}{r}}) + A_{\eta LM}\frac{1}{k}\nabla\times h_L(kr)\underset{\sim}{X}_{LM}(\hat{\underset{\sim}{r}})\right] \quad (5\text{-}6b)$$

where the Hankel functions of the first kind, $h_L(kr)$, ensure the correct behavior of the field at infinity: eqs. (5-6), indeed, contain only outgoing spherical waves. Now we recall that, at the surface of the sphere, the tangential components of $\underset{\sim}{E}$ and $\underset{\sim}{B}$ should be continuous as well as the radial component of $\underset{\sim}{B}$, while the radial component of $\underset{\sim}{E}$ should satisfy

$$n^2\underset{\sim}{E}_1\cdot\hat{\underset{\sim}{r}} = \underset{\sim}{E}_2\cdot\hat{\underset{\sim}{r}}$$

where the index 1 refers to the interior of the sphere.

By imposing the above boundary conditions we get, for each L,M, six equations among which C_{LM} and D_{LM}, the coefficients of the internal field, are easily eliminated. The remaining equations then yield for $A_{\eta LM}$ and $B_{\eta LM}$ the equations

$$A_{\eta LM} = W_{\eta LM}\left[\frac{j_L(kr)\frac{d}{dr}(rR_L) - R_L\frac{d}{dr}(rj_L(kr))}{h_L(kr)\frac{d}{dr}(rR_L) - R_L\frac{d}{dr}(rh_L(kr))}\right]_{r=b} = W_{\eta LM}\,\mathcal{R}_L \tag{5-7a}$$

$$B_{\eta LM} = \eta W_{\eta LM}\left[\frac{j_L(kr)\frac{d}{dr}(rS_L) - m^2 S_L\frac{d}{dr}(rj_L(kr))}{h_L(kr)\frac{d}{dr}(rS_L) - m^2 S_L\frac{d}{dr}(rh_L(kr))}\right]_{r=b} =$$

$$= \eta W_{\eta LM}\,\mathcal{S}_L. \tag{5-7b}$$

Equations (5-7) solve completely our problem since all the quantities of interest can be expressed in terms of the A and B coefficients. In particular the scattering, absorption and total cross sections are given by

$$\sigma_\eta^{(sc)} = \frac{2\pi^2}{k^2}\sum_{LM}\left[|A_{\eta LM}|^2 + |B_{\eta LM}|^2\right] \tag{5-8a}$$

$$\sigma_\eta^{(abs)} = \frac{2\pi^2}{k^2}\sum_{LM}\left[2 - |A_{\eta LM}+1|^2 - |B_{\eta LM}+1|^2\right] \tag{5-8b}$$

$$\sigma_\eta^{(tot)} = \frac{4\pi^2}{k^2}\sum_{LM}\mathcal{R}e\left(A_{\eta LM} + B_{\eta LM}\right) \tag{5-8c}$$

where $\mathcal{R}e$ denotes the real part[3]. Note that for a sphere the dependence of the A's, B's and σ's on the polariza-

tion index, η. However, we will see in the next section that the cross section of a cluster of spheres can still be cast in the form of eqs. (5-8), but with an actual dependence on the polarization of the incident wave.

6. Scattering from a cluster of spheres.

As is well known, the scatterers in the most common aerosols are far from spherical and their properties cannot be described by Mie theory but to low approximation. We shall, therefore, introduce a model scatterer whose features allow to fit the properties even of highly asymmetric objects, although their scattered field can be calculated without too much computational effort. We define, in fact, our model scatterer as a cluster of N nonmagnetic spheres whose centres lie at $\underline{R}_\alpha$ and whose radia and (possibly complex and radially symmetric) refractive indexes are b_α and n_α, respectively. The field inciding on the cluster is assumed to be the plane wave described by eqs. (5-4), while the scattered field will be written as

$$\underset{\sim}{E}^{(s)}_\eta = \sum_\alpha \sum_{LM} \left[A^\alpha_{\eta LM}\, h_L(kr_\alpha) \underset{\sim}{X}_{LM}(\hat{r}_\alpha) + B^\alpha_{\eta LM} \frac{1}{k} \nabla \times h_L(kr_\alpha) \underset{\sim}{X}_{LM}(\hat{r}_\alpha) \right] \quad (6\text{-}1a)$$

$$i\,\underset{\sim}{B}^{(s)}_\eta = \sum_\alpha \sum_{LM} \left[B^\alpha_{\eta LM}\, h_L(kr_\alpha) \underset{\sim}{X}_{LM}(\hat{r}_\alpha) + A^\alpha_{\eta LM} \frac{1}{k} \nabla \times h_L(kr_\alpha) \underset{\sim}{X}_{LM}(\underset{\sim}{r}_\alpha) \right] \quad (6\text{-}1b)$$

with $\underset{\sim}{r}_\alpha = \underset{\sim}{r} - \underset{\sim}{R}_\alpha$, i.e. as a superposition of the fields scattered from the single spheres. The coefficients $A^\alpha_{\eta LM}$ and $B^\alpha_{\eta LM}$, however, are not merely given by eqs. (5-7)

but are calculated so as to account for multiple scatterings among the spheres. In other words, the field incident on the α-th sphere is assumed to be that of the incoming plane wave plus that previously scattered by all other spheres. This effect is achieved by rewriting both the incident and the scattered fields in terms of VSH's centered at $\underline{R}_\alpha$ through the addition theorem of sect. 4. We get

$$\mathbf{E}^{(i)}_{\eta}=\sum_{LM} W_{\eta LM}(\hat{\mathbf{k}})\Big\{\sum_{L'M'}\Big[\mathcal{J}^{\alpha}_{L'M'LM}\, j_{L'}(kr_\alpha)\,\mathbf{X}_{L'M'}(\hat{\mathbf{r}}_\alpha)+\mathcal{L}^{\alpha}_{L'M'LM}\,\frac{1}{k}\nabla\times j_{L'}(kr_\alpha)\,\mathbf{X}_{L'M'}(\hat{\mathbf{r}}_\alpha)\Big]$$
$$+\eta\sum_{L'M'}\Big[\mathcal{L}^{\alpha}_{L'M'LM}\, j_{L'}(kr_\alpha)\,\mathbf{X}_{L'M'}(\hat{\mathbf{r}}_\alpha)+\mathcal{J}^{\alpha}_{L'M'LM}\,\frac{1}{k}\nabla\times j_{L'}(kr_\alpha)\,\mathbf{X}_{L'M'}(\hat{\mathbf{r}}_\alpha)\Big]\Big\} \quad (6\text{-}2)$$

$$\mathbf{E}^{(s)}_{\eta}=\sum_{LM}\Big\{A^{\alpha}_{\eta LM}\, h_L(kr_\alpha)\,\mathbf{X}_{LM}(\hat{\mathbf{r}}_\alpha)+\mathcal{B}^{\alpha}_{\eta LM}\,\frac{1}{k}\nabla\times h_L(kr_\alpha)\,\mathbf{X}_{LM}(\hat{\mathbf{r}}_\alpha)+$$
$$+\sum_{\beta}\sum_{L'M'}\Big[A^{\beta}_{\eta LM}\Big(\mathcal{H}^{\alpha\beta}_{L'M'LM}\, j_{L'}(kr_\alpha)\,\mathbf{X}_{L'M'}(\hat{\mathbf{r}}_\alpha)+\mathcal{K}^{\alpha\beta}_{L'M'LM}\,\frac{1}{k}\nabla\times j_{L'}(kr_\alpha)\,\mathbf{X}_{L'M'}(\hat{\mathbf{r}}_\alpha)\Big)$$
$$+\mathcal{B}^{\beta}_{\eta LM}\Big(\mathcal{K}^{\alpha\beta}_{L'M'LM}\, j_{L'}(kr_\alpha)\,\mathbf{X}_{L'M'}(\hat{\mathbf{r}}_\alpha)+\mathcal{H}^{\alpha\beta}_{L'M'LM}\,\frac{1}{k}\nabla\times j_{L'}(kr_\alpha)\,\mathbf{X}_{L'M'}(\hat{\mathbf{r}}_\alpha)\Big)\Big]\Big\}, \quad (6\text{-}3)$$

and analogous equations for $i\mathbf{B}^{(i)}_\eta$ and $i\mathbf{B}^{(s)}_\eta$. The field within the α-th sphere is assumed in the form of eqs. (5-6) with $\underline{r}_\alpha$ substituted to $\underline{r}$.

Now, we take the dot product of eqs. (6-2), (6-3) and (5-6) in turn with $\hat{\mathbf{r}}_\alpha Y^*_{\ell m}(\hat{\mathbf{r}}_\alpha)$, $\mathbf{X}^*_{\ell m}(\hat{\mathbf{r}}_\alpha)$ and $\hat{\mathbf{r}}_\alpha\times\mathbf{X}^*_{\ell m}(\hat{\mathbf{r}}_\alpha)$ and get the radial and tangential components of the fields at the surface of the α-th sphere. Imposition of the boundary conditions and integration over the angles yield

for each α, l, m, six equations among which $C^{\alpha}_{\eta LM}$ and $D^{\alpha}_{\eta LM}$, the coefficients of the internal field are easily eliminated. This possibility allows to get, for each α, l, m, two equations involving only the A's and B's as unknowns

$$\sum_{\beta}\sum_{LM}\left\{\left(\delta_{\alpha\beta}\delta_{Ll}\delta_{Mm}[\mathcal{R}^{\beta}_{L}]^{-1}+\mathcal{H}^{\alpha\beta}_{lmLM}\right)A^{\beta}_{\eta LM}+\mathcal{K}^{\alpha\beta}_{lmLM}B^{\beta}_{\eta LM}\right\}=$$

$$=-\sum_{LM}W_{\eta LM}(\hat{\underline{k}})\,\mathcal{P}^{\alpha}_{\eta, lmLM} \qquad (6\text{-}4a)$$

$$\sum_{\beta}\sum_{LM}\left\{\left(\delta_{\alpha\beta}\delta_{Ll}\delta_{Mm}[\mathcal{J}^{\beta}_{L}]^{-1}+\mathcal{H}^{\alpha\beta}_{lmLM}\right)B^{\beta}_{\eta LM}+\mathcal{K}^{\alpha\beta}_{lmLM}A^{\beta}_{\eta LM}\right\}=$$

$$=-\sum_{LM}W_{\eta LM}(\hat{\underline{k}})\,\mathcal{Q}^{\alpha}_{\eta, lmLM} \qquad (6\text{-}4b)$$

In eqs. (6-4) we define

$$\mathcal{P}^{\alpha}_{\eta, lmLM}=\mathcal{J}^{\alpha}_{lmLM}+\eta\,\mathcal{L}^{\alpha}_{lmLM} \qquad (6\text{-}5a)$$

$$\mathcal{Q}^{\alpha}_{\eta, lmLM}=\mathcal{L}^{\alpha}_{lmLM}+\eta\,\mathcal{J}^{\alpha}_{lmLM} \qquad (6\text{-}5b)$$

while $\mathcal{R}^{\alpha}_{l}$ and $\mathcal{J}^{\alpha}_{l}$ are still defined as in eqs. (5-7) with obvious change of the arguments. The system composed of equations (6-4) for all values of α, l, m, allows a complete and unique determination of the scattered field and thus of all the quantities of interest. As an example, to calculate the cross sections of the cluster we rewrite the scattered field in terms of VSH's centered at a single site, say $\underline{R}_0$, through application of the addition theorem of sect. 4. We get for the electric field

$$\underset{\sim}{E}^{(s)}_{\eta}=\sum_{\alpha}\sum_{LM}\left\{A^{\alpha}_{\eta LM}\sum_{L'M'}\left[\mathcal{J}^{0\alpha}_{L'M'LM}h_{L'}(kr_0)\underset{\sim}{X}_{L'M'}(\hat{\underset{\sim}{r}}_0)+\mathcal{L}^{0\alpha}_{L'M'LM}\frac{1}{k}\nabla\times h_{L'}(kr_0)\underset{\sim}{X}_{L'M'}(\hat{\underset{\sim}{r}}_0)\right]\right.$$

$$+ B^{\alpha}_{\eta LM} \sum_{L'M'} \left[\mathcal{L}^{0\alpha}_{L'M'LM} h_{L'}(kr_0) \underset{\sim}{X}_{L'M'}(\hat{\underset{\sim}{r}}_0) + \mathcal{J}^{0\alpha}_{L'M'LM} \frac{1}{k} \nabla \times h_{L'}(kr_0) \underset{\sim}{X}_{L'M'}(\hat{\underset{\sim}{r}}_0) \right] \Big\} \quad (6\text{-}6)$$

with $\underline{r}_0 = \underline{r} - \underline{R}_0$, and an analogous expression for $i\underset{\sim}{B}^{(s)}_{\eta}$.
Now, by defining

$$\widetilde{A}_{\eta L'M'} = \sum_{\alpha} \sum_{LM} \left[A^{\alpha}_{\eta LM} \mathcal{J}^{0\alpha}_{L'M'LM} + B^{\alpha}_{\eta LM} \mathcal{L}^{0\alpha}_{L'M'LM} \right]$$

$$\widetilde{B}_{\eta L'M'} = \sum_{\alpha} \sum_{LM} \left[A^{\alpha}_{\eta LM} \mathcal{L}^{0\alpha}_{L'M'LM} + B^{\alpha}_{\eta LM} \mathcal{J}^{0\alpha}_{L'M'LM} \right]$$

the scattered field can be written in the form of that scattered by a single sphere, so that the cross sections of the cluster are still given by eqs. (5-8) with $\widetilde{A}$'s and $\widetilde{B}$'s substituted for A's and B's, respectively.
It is to be noted that, since the cluster lecks the spherical symmetry, the cross sections are actually dependent on the polarization index, η . Furthermore we notice that the choice of the point $\underline{R}_0$ is quite arbitrary but that according to sect. 4, eq. (6-6) is valid for $r_0 \geq |\underset{\sim}{R}_{\alpha} - \underset{\sim}{R}_0|$ for any α , i.e. in the region external to a sphere centered at $\underline{R}_0$ and including the whole cluster. The radius of this sphere can be minimized by choosing $\underline{R}_0$ at the centre of mass of the cluster, but the choice is not crytical for the scattered field is always observed at distances larger than the size of the cluster.

7. Convergency.

The method described in the preceding sections does not require any approximation but for the multipolar expansion of the scattered field, eqs. (6-1). It is therefore of fundamental importance for the feasibility of the method itself to discuss the rate of convergence of these expansions. To this end let us rewrite the system of eqs. (6-4) matrixwise as

$$\begin{vmatrix} \underset{\sim}{\mathcal{R}}^{-1}+\underset{\sim}{\mathcal{H}} & \underset{\sim}{\mathcal{K}} \\ \underset{\sim}{\mathcal{K}} & \underset{\sim}{\mathcal{J}}^{-1}+\underset{\sim}{\mathcal{H}} \end{vmatrix} \begin{vmatrix} \underset{\sim}{A} \\ \underset{\sim}{B} \end{vmatrix} = - \begin{vmatrix} \underset{\sim}{P} \\ \underset{\sim}{Q} \end{vmatrix} \qquad (7\text{-}1)$$

Equation (7-1) allows to identify the matrix on its left hand side as the inverse of the electromagnetic T-matrix of the whole cluster[2)]. Of course it is not diagonal on account of the lack of spherical symmetry of the cluster as a whole. However, the matrices $\underset{\sim}{\mathcal{R}}, \underset{\sim}{\mathcal{J}}, \underset{\sim}{\mathcal{H}}$ and $\underset{\sim}{\mathcal{K}}$ have an interesting physical meaning of thir own and their analical behavior determines the rate of convergency of the scattered field, as we are going to discuss.
The diagonal metrices $\underset{\sim}{\mathcal{R}}$ and $\underset{\sim}{\mathcal{J}}$ are the direct sum of the matrices $\underset{\sim}{\mathcal{R}}^{\alpha}$ and $\underset{\sim}{\mathcal{J}}^{\alpha}$ defined according to eqs. (5-7), which account for the scattering power of the α-th sphere in the absence of any other scatterer. Thus the presence in the cluster of more than one scatterer is accounted for not only by the $\underset{\sim}{\mathcal{R}}^{\beta}$ and $\underset{\sim}{\mathcal{J}}^{\beta}$ with $\beta \neq \alpha$ but also by the matrices $\underset{\sim}{\mathcal{H}}$ and $\underset{\sim}{\mathcal{K}}$ which couple to each other all the

spheres in the cluster. Indeed, as shown in sect. 4, $\mathcal{H}^{\alpha\beta}_{lmLM}$ and $\mathcal{K}^{\alpha\beta}_{lmLM}$ are the matrix elements of the free space dyadic Green function and thus describe the propagation to site α of the waves scattered by site β . This remark fully justifies our previous statement that all multiple scattering processes are accounted for in the present theory.

As regards the rate of convergenncy, we remark that it is expected to be fairly good even when the cluster is not small in comparison with the incident wavelenght, provided $kb_\alpha \ll 1$ for any α . Under this condition, $\mathcal{R}^\alpha_l$ and $\mathcal{S}^\alpha_l$ decrease rapidly with increasing l so that $\mathcal{R}^\alpha_1$ and $\mathcal{S}^\alpha_1$ are quite sufficient to describe the field scattered by the α-th sphere in the absence of any other scatterer, even when n_α is not close to unity[17,19]. The rate of convergence thus depends on the behaviour of $\mathcal{H}^{\alpha\beta}_{lmLM}$ and $\mathcal{K}^{\alpha\beta}_{lmLM}$. Now, one easily sees from their definition, that thir order of magnitude is determined by the Gaunt integrals, I_λ , and on the spherical Hankel functions $h_\lambda(kR_{\alpha\beta})$. The I_λ -integrals do not vanish only for $|L-l| \leq \lambda \leq L+l$ and decrease very rapidly with increasing λ[20]. Thus, although the imaginary part of h_λ , $n_\lambda(kR_{\alpha\beta})$, tends to increase when $\lambda > kR_{\alpha\beta}$, the eventual effect is to decrease the magnitude of both $\mathcal{H}^{\alpha\beta}_{lmLM}$ and $\mathcal{K}^{\alpha\beta}_{lmLM}$ with increasing l, L and $R_{\alpha\beta}$. This behaviour is to be expected for, when the intersphere distance is very large, the present theory should reduce to that of

the scattering from N spherical scatterers without any multiple scattering effect. As a consequence it is reasonable to expect that our approach converge well by truncating the expansion, eqs. (6-1), of the scattered field at $L=L_M=3$. However, the order of the system (7-1) is $d_M= 2N(L_M+1)^2-2N$, so that we have $d_3=30N$, a very high number even for small clusters. Nevertheless, if the cluster posses symmetry properties, as is the case for actual molecules, we shall use group theory to put the system (7-1) in factorized form, as will be shown in the next sections.

8. Symmetrization.

We assume that he cluster is left invariant by the transformations of a group $\mathcal{G}$ of order g. The effect of these transformations is to permute among themselves the spheres in the cluster but, in general, not all the spheres are linked to each other by an operation of $\mathcal{G}$ [21]. Therefore we partition the cluster into sets of spheres which are transformed to each other by the operations of the group. Of course this does not imply a renumbering of the spheres but only that we associate to each site index, α, the appropriate set index, σ.

In order to get the system of eqs. (6-4) in factorized form we have to expand both the incident and the scattered field in terms of combinations of VSH's transforming according to the rows of the irreducible

representation of $\mathcal{G}$. To this end we recall that, as shown in sect. 3, the VSH's transform according to the representation $D^{(L)}$ of the full rotation group. Therefore, if S is an operation of such that

$$S\underline{R}_\alpha = \underline{R}_\beta$$

with α and β in the same set, of course, and O_S is the associated operator, then[22)]

$$\mathcal{O}_S f_L(kr_\alpha)\underset{\sim}{X}_{LM}(\hat{\underline{r}}_\alpha) = \sum_{M'} f_L(kr_\beta)\mathcal{D}^{(L)}_{M'M}(S)\underset{\sim}{X}_{LM'}(\hat{\underline{r}}_\beta) \qquad (8\text{-}1a)$$

$$\mathcal{O}_S \nabla\times f_L(kr_\alpha)\underset{\sim}{X}_{LM}(\hat{\underline{r}}_\alpha) = \sum_{M'} \nabla\times f_L(kr_\beta)\mathcal{D}^{(L)}_{M'M}(S)\underset{\sim}{X}_{LM'}(\hat{\underline{r}}_\beta) \qquad (8\text{-}1b)$$

provided S is a proper operation. When S is an improper operation we must take account that $f_L\underline{X}_{LM}$ and $\nabla\times f_L\underline{X}_{LM}$ have opposite parity, so that eq. (8-1a) must be multiplied by $(-)^L$ and eq. (8-1b) by $(-)^{L+1}$ and the argument of $D^{(L)}$ must be understood as the proper rotational part of S. As a consequence, to get the symmetrized combinations of VSH's we must apply the projection operators

$$\mathbb{P}^{\nu}_{pq} = (g_\nu/g)\sum_S \mathcal{D}^{(\nu)*}_{pq}(S)\,\mathcal{O}_S \qquad (8\text{-}2)$$

both to the magnetic and to the electric 2^L-poles. Therefore we write

$$\underset{\sim}{H}^{\nu p\sigma}_{NL} = \sum_{\alpha\in\sigma}\sum_{M\in N} a^{\nu p\alpha}_{NLM}\, h_L(kr_\alpha)\underset{\sim}{X}_{LM}(\hat{\underline{r}}_\alpha) \qquad (8\text{-}3a)$$

and

$$\underset{\sim}{K}^{\nu p\sigma}_{NL} = \sum_{\alpha\in\sigma}\sum_{M\in N} b^{\nu p\alpha}_{NLM}\,\frac{1}{k}\,\nabla\times h_L(kr_\alpha)\underset{\sim}{X}_{LM}(\hat{\underline{r}}_\alpha) \qquad (8\text{-}3b)$$

for the combinations of magnetic and electric multipoles centered at sites of the σ-th set. The superscripts ν,p indicate that the combination belongs to the p-th row

of the ν-th irreducible representation and the index N recalls, when appropriate, that one can get more than one set of basis functions for a given L. Now the field scattered by the cluster can be written as

$$\underset{\sim}{E}_{\eta}^{(s)} = \sum_{\nu p}\sum_{\sigma}\sum_{L}\Big[\sum_{N} \mathcal{A}_{\eta NL}^{\nu p\sigma}\, \underset{\sim}{H}_{NL}^{\nu p\sigma} + \sum_{N'} \mathcal{B}_{\eta N'L}^{\nu p\sigma}\, \underset{\sim}{K}_{N'L}^{\nu p\sigma}\Big] \qquad (8\text{-}4)$$

with a similar expression for $i\underset{\sim}{B}_{\eta}^{(s)}$. We notice that we work with unitary irreducible representations, as shown by the structure of the projection operators, eq. (8-2), and the coefficients a's and b's have the property

$$\sum_{\alpha\sigma}\sum_{M}(a_{NLM}^{\nu p\alpha})^{*}(a_{N'LM}^{\nu p\alpha}) = \delta_{NN'}\ ,\ \sum_{\alpha\sigma}\sum_{M}(b_{NLM}^{\nu p\alpha})^{*}(b_{N'LM}^{\nu p\alpha}) = \delta_{NN'} \quad (8\text{-}5)$$

We have now to decompose the incident field into parts belonging to the rows of the irreducible representations of $\mathcal{G}$. To do this we use the completeness property[23)]

$$\sum_{\nu p} \mathbb{P}_{pp}^{\nu} = 1$$

and write

$$\underset{\sim}{E}_{\eta}^{(i)} = \sum_{LM} W_{\eta LM}(\hat{\underset{\sim}{k}})\sum_{\nu p}\mathbb{P}_{pp}^{\nu}\big[j_L(kr)\underset{\sim}{X}_{LM}(\hat{\underset{\sim}{r}}) + \eta\frac{1}{k}\nabla\times j_L(kr)\underset{\sim}{X}_{LM}(\hat{\underset{\sim}{r}})\big]$$

$$= \sum_{\nu p}\sum_{LM} W_{\eta LM}(\underset{\sim}{k})\,\big[\underset{\sim}{J}_{LM}^{\nu p} + \eta\,\underset{\sim}{L}_{LM}^{\nu p}\big] \qquad (8\text{-}6)$$

where

$$\underset{\sim}{J}_{LM}^{\nu p} = (g_{\nu}/g)\sum_{S} D_{pp}^{(\nu)*}(S)\sum_{M'} D_{M'M}^{(L)}(S)\, j_L(kr)\underset{\sim}{X}_{LM'}(\hat{\underset{\sim}{r}}) =$$

$$= \sum_{M'} c_{LMM'}^{\nu p}\, j_L(kr)\underset{\sim}{X}_{LM'}(\underset{\sim}{r}) \qquad (8\text{-}7a)$$

$$\underset{\sim}{L}_{LM}^{\nu p} = \sum_{M'} d_{LMM'}^{\nu p}\,\frac{1}{k}\nabla\times j_L(kr)\underset{\sim}{X}_{LM'}(\hat{\underset{\sim}{r}}) \qquad (8\text{-}7b)$$

The analogous equation for $i\underset{\sim}{B}_\eta^{(i)}$ is easily obtained through the relation

$$i\,\underset{\sim}{B}_\eta^{(i)} = \eta\,\underset{\sim}{E}_\eta^{(i)}$$

The field within the spheres need not be symmetrized for reasons that will become apparent later. The internal field is therefore still given by

$$\underset{\sim}{E}_\eta^{(t)\alpha} = \sum_{LM}\left[C^\alpha_{\eta LM}\,R^\alpha_L(r_\alpha)\underset{\sim}{X}_{LM}(\hat{\underset{\sim}{r}}_\alpha) + \frac{1}{M_\alpha^2}D^\alpha_{\eta LM}\frac{1}{k}\nabla\times S_L(r_\alpha)\underset{\sim}{X}_{LM}(\hat{\underset{\sim}{r}}_\alpha)\right] \quad (8\text{-}8a)$$

$$i\underset{\sim}{B}_\eta^{(t)\alpha} = \sum_{LM}\left[D^\alpha_{\eta LM}\,S_L(r_\alpha)\underset{\sim}{X}_{LM}(\hat{\underset{\sim}{r}}_\alpha) + C^\alpha_{\eta LM}\frac{1}{k}\nabla\times R_L(r_\alpha)\underset{\sim}{X}_{LM}(\hat{\underset{\sim}{r}}_\alpha)\right] \quad (8\text{-}8b)$$

At this stage we can write the system for the coefficients $\mathcal{A}_{NL}^{\nu p\sigma}$ and $\mathcal{B}_{N'L}^{\nu p\sigma}$ through the same procedure we used in sect. 6. We rewrite eq. (8-4) and (8-6) in terms of VSH's centered at the site α belonging to the σ-th set by means of the addition theorem of sect. 4. Then we dot multiply the resulting equations, as well as equations (8-8), in turn by $\hat{\underset{\sim}{r}}_\alpha Y_{lm}(\hat{\underset{\sim}{r}}_\alpha)$, $\underset{\sim}{X}_{lm}(\hat{\underset{\sim}{r}}_\alpha)$ and $\hat{\underset{\sim}{r}}_\alpha\times\underset{\sim}{X}_{lm}(\hat{\underset{\sim}{r}}_\alpha)$ and get the radial and the tangential components of the fields. Imposition of the boundary conditions and integration over the angle yield, for each ν, p, α, six equations among which $C^\alpha_{\eta LM}$ and $D^\alpha_{\eta LM}$, the coefficients of the internal field, can be easily eliminated. This circumstance on one hand clarifies the inessentiality of the symmetrization of the internal field, on the other hand yields, for each ν, p, α, two equations involving only the $\mathcal{A}$'s and the $\mathcal{B}$'s as unknowns:

$$\sum_L \sum_\tau \sum_{\beta \in \tau} \Big\{ \sum_N \sum_{M \in N} \big(\delta_{L\ell}\, \delta_{Mm}\, \delta_{\alpha\beta} [\mathcal{R}_L^\beta]^{-1} + \mathcal{H}^{\alpha\beta}_{\ell m L M} \big)\, a^{\nu p \beta}_{NLM}\, \mathcal{A}^{\nu p \tau}_{\eta N L} +$$

$$+ \sum_{N'} \sum_{\bar{M} \in N'} \mathcal{K}^{\alpha\beta}_{\ell m L \bar{M}}\, b^{\nu p \beta}_{N' L \bar{M}}\, \mathcal{B}^{\nu p \tau}_{\eta N' L} =$$

$$= - \sum_{LM} \sum_{M'} W_{\eta L M}(\hat{k}) \big[c^{\nu p}_{LMM'}\, \mathcal{J}^{\alpha}_{\ell m L M'} + \eta\, d^{\nu p}_{LMM'}\, \mathcal{L}^{\alpha}_{\ell m L M'} \big] \qquad (8\text{-}9a)$$

$$\sum_L \sum_\tau \sum_{\beta \in \tau} \Big\{ \sum_{N'} \sum_{\bar{M} \in N'} \big(\delta_{L\ell}\, \delta_{\bar{M}m}\, \delta_{\alpha\beta} [\mathcal{S}_L^\beta]^{-1} + \mathcal{H}^{\alpha\beta}_{\ell m L \bar{M}} \big)\, b^{\nu p \beta}_{N' L \bar{M}}\, \mathcal{B}^{\nu p \tau}_{\eta N' L} +$$

$$+ \sum_N \sum_{M \in N} \mathcal{K}^{\alpha\beta}_{\ell m L \bar{M}}\, a^{\nu p \beta}_{NLM}\, \mathcal{A}^{\nu p \tau}_{\eta N L} =$$

$$= - \sum_{LM} \sum_{M'} W_{\eta L M}(\hat{k}) \big[c^{\nu p}_{LMM'}\, \mathcal{L}^{\alpha}_{\ell m L M'} + \eta\, d^{\nu p}_{LMM'}\, \mathcal{J}^{\alpha}_{\ell m L M'} \big] \qquad (8\text{-}9b)$$

It may seem that the system of equations (8-9) solve our problem, but, apart from its rather asymmetrical form, it is still not completely factorized. However we remark that the spheres within a given set are identical to each other so that $\mathcal{R}_L^\alpha$ and $\mathcal{S}_L^\alpha$ do not actually depend on the site index, α, but rather by the set index, σ. Therefore we can multiply eq. (8-9a) by $(a^{\nu p \alpha}_{n\ell m})^*$ and eq. (8-9b) by $(b^{\nu p \alpha}_{n'\ell m})^*$ and sum over the α's belonging to σ and over m. The orthogonality relations, eqs. (8-5), then yield for each ν, p, τ, the equations

$$\sum_s \big[\delta_{rs} [\mathcal{R}_s]^{-1} + \mathcal{H}^{\nu}_{rs}(m) \big] \mathcal{A}^{\nu p}_{\eta s} + \sum_{s'} \mathcal{K}^{\nu}_{rs'}(m,e)\, \mathcal{B}^{\nu p}_{\eta s'} = -\mathcal{P}^{\nu p}_{\eta r} \qquad (8\text{-}10a)$$

$$\sum_{s'} \big[\delta_{r's'} [\mathcal{S}_{s'}]^{-1} + \mathcal{H}^{\nu}_{r's'}(e) \big] \mathcal{B}^{\nu p}_{\eta s'} + \sum_{s} \mathcal{K}^{\nu}_{r's}(e,m)\, \mathcal{A}^{\nu p}_{\eta s} = -\mathcal{Q}^{\nu p}_{\eta r'} \qquad (8\text{-}10b)$$

where, for the sake of semplicity, we put $r \equiv (\sigma, l, n)$, $s \equiv (\tau, L, N)$, $r' \equiv (\sigma, l, n')$, $s' \equiv (\tau, L, N')$ and define

$$\mathcal{H}^{\nu}_{rs}(m) = \sum_{\alpha m} \sum_{\beta M} (a^{\nu p \alpha}_{n l m})^* \mathcal{H}^{\alpha\beta}_{lmLM} \, a^{\nu p \beta}_{NLM} \qquad (8\text{-}11a)$$

$$\mathcal{K}^{\nu}_{rs}(m,e) = \sum_{\alpha m} \sum_{\beta M} (a^{\nu p \alpha}_{n l m})^* \mathcal{K}^{\alpha\beta}_{lmLM} \, b^{\nu p \beta}_{NLM} \qquad (8\text{-}11b)$$

with an obvious meaning of the parameters e,m. The quantities $\mathcal{H}^{\nu}_{rs}(e)$ and $\mathcal{K}^{\nu}_{rs}(e,m)$ are identical to $\mathcal{H}^{\nu}_{rs}(m)$ and $\mathcal{K}^{\nu}_{rs}(m,e)$, respectively, but for the mutual exchange of the a's with the b's. Moreover

$$\mathcal{P}^{\nu p}_{\eta r} = \sum_{LM} \sum_{\alpha m} \sum_{M'} W_{\eta LM}(\hat{k}) (a^{\nu p \alpha}_{n l m})^* \left[c^{\nu p}_{LMM'} \mathcal{J}^{\alpha}_{lmLM'} + \eta \, d^{\nu p}_{LMM'} \mathcal{L}^{\alpha}_{lmLM'} \right] \qquad (8\text{-}12a)$$

$$Q^{\nu p}_{\eta r} = \sum_{LM} \sum_{\alpha m} \sum_{M'} W_{\eta LM}(\hat{k}) (b^{\nu p \alpha}_{n l m})^* \left[c^{\nu p}_{LMM'} \mathcal{L}^{\alpha}_{lmLM'} + \eta \, d^{\nu p}_{LMM'} \mathcal{J}^{\alpha}_{lmLM'} \right] . \qquad (8\text{-}12b)$$

We remark that on the left hand side of eqs. (8-10) and (8-11) the superscript p on $\mathcal{H}^{\nu}_{rs}$ and $\mathcal{K}^{\nu}_{rs}$ is missing. As will be shown later, these quantities are actually independent of the row index, p, which has accordingly been dropped. Anyway the systems of equations (8-10) solve completely our scattering problem. Indeed, direct comparison of eqs. (6-1) with eqs. (8-4) yields

$$A^{\alpha}_{\eta LM} = \sum_{\nu p} \sum_{N} \mathcal{A}^{\nu p \sigma}_{\eta NL} \, a^{\nu p \alpha}_{NLM} \quad , \quad B^{\alpha}_{\eta LM} = \sum_{\nu p} \sum_{N} \mathcal{B}^{\nu p \sigma}_{\eta NL} \, b^{\nu p \alpha}_{NLM}$$

Threfore all the properties of interest can be expressed in terms of $\mathcal{A}^{\nu p \sigma}_{\eta NL}$ and $\mathcal{B}^{\nu p \sigma}_{\eta NL}$, the coefficients of the symmetrized expansion of the scattered field.

9. Discussion.

The consequences of the factorization effected by group theory can be better discussed if we write the system with a given ν, p in matrix form:

$$\begin{vmatrix} \underset{\sim}{\mathcal{R}}^{-1} + \underset{\sim}{\mathcal{H}}^{\nu}(m) & \mathcal{K}^{\nu}(m,e) \\ \mathcal{K}^{\nu}(e,m) & \mathcal{S}^{-1} + \mathcal{H}(e) \end{vmatrix} \begin{vmatrix} \underset{\sim}{\mathcal{A}}^{\nu p} \\ \mathcal{B}^{\nu p} \end{vmatrix} = - \begin{vmatrix} \underset{\sim}{P}^{\nu p} \\ Q^{\nu p} \end{vmatrix} \qquad (9\text{-}1)$$

As equation (9-1) has the same overall structure of eq. (7-1), the matrix on its left is still the inverse of the electromagnetic T-matrix for the whole cluster, or better that part of the inverse T-matrix which belongs to the ν-th irreducible representation of $\mathcal{G}$. This means that, although the lack of spherical symmetry does not allow to get a diagonal T-matrix, nevertheless group theory effects the decomposition of the whole scattering process into <u>modes of scattering</u> belonging to the irreducible representations of $\mathcal{G}$. The dependence on the row index of the inhomogeneity of eq. (9-1) forces us to solve <u>all</u> the systems arising from the factorization procedure, in contrast to the case of secular determinants in which one need solve only one system per representation. However, as explicitly indicated by the omission of the superscript p, the T-matrix for the ν-th mode of scattering does not depend on p, as we shall show presently. The p-independence of $\underset{\sim}{\mathcal{R}}$ and $\underset{\sim}{\mathcal{S}}$ follows from the very definition of their matrix elements, eq. (5-7). In turn the

elments of the matrices $\underset{\sim}{\mathcal{H}}^{\nu}(m), \underset{\sim}{\mathcal{H}}^{\nu}(e), \mathcal{K}^{\nu}(m,e)$ and $\mathcal{K}^{\nu}(e,m)$ are the symmetrized counterparts of the quantities $\mathcal{H}^{\alpha\beta}_{lmLM}$ and $\mathcal{K}^{\alpha\beta}_{lmLM}$, which, as shown in sect. 4b, are the matrix elements of the free space dyadic Green function in the site and angular momentum representation. The p-independence of $\mathcal{H}^{\nu}(m), \mathcal{H}^{\nu}(e), \mathcal{K}^{\nu}(m,e)$ and $\mathcal{K}^{\nu}(e,m)$ is then a direct consequence of the inveriance of the Green function under the symmetry operations. Therefore the whole T-matrix for the ν-th mode of scattering turns out to be independent of the row index p. This circumstance greatly reduces the computational work in the case of multidimensional representations. However, we remark that the extent of the factorization cannot be stated in general. In fact it depends not only on the number of L-values included in the multipolar expansion of the fields and on the number of spheres in the cluster, but also on the structure of the symmetry group. The effect of the factorization can thus be illustrated only through examles. Table I reports the order of the systems to be solved for a cluster of 5 spheres with point group T_d (the CH_4 molecule and the SO_4^{++} ion have just this structure). Although table I considers the case in which terms up to L=4 are included in the expansion of the scattered field, from the discussion of sect. 7 we expect that terms up to L=3 are sufficient to get fairly converged values of the field. The usefulnes of group theroy requires no further comment.

TABLE I

L_M	1	2	3	4
A_1	1	2	6	10
A_2	1	2	6	10
E	2	8	12	20
F_1	4	10	19	30
F_2	4	10	19	30
U	30	80	150	240

Table caption

Dimension of the symmetrized and of the unsymmetrized systems for L_M up to 4 for a cluster of 5 spheres with point group T_d. The entry U means unsymmetrized while the other entries indicate the irreducible representations in the notation of ref. 25.

Appendix A

The program SCVSH: a user's gide.

This appendix is meant to be a user's guide to SCVSH, a program designed to generate symmetry adapted combinations of Vector Spherical Harmonics and to decompose a given VSH into parts belonging to the rows of the irreducible representations of a point group $\mathcal{G}$. The relevant formulas are reported in sect. 8 of the main text. Here we describe the input quantities and the line of operation of the soubroutines.

A1. Input data.

All the input data are read in the main program. Their sequence and FORMATS are as follows.

CARD 1 (3A4,8X,3I5)

IDSTR,IDG,NOPS,NINV,NREP

IDSTR The name identifying the structure of the cluster.

IDG The name of the symmetry group, $\mathcal{G}$.

NOPS Number of operations in $\mathcal{G}$.

NINV Number of pure rotations in $\mathcal{G}$.

NREP Number of the irreducible representations.

CARD 2 (16I5)

IDREP(NP),NDIM(NP)

IDREP Name of the NP-th irreducible representation.

NDIM Dimension of the NP-th irreducible represen-

tation of $\mathcal{G}$.

CARD 3 (8F10.7)

DDN(NP,NR,NCOL)

DDN Matrix elements of the first row of the NP-th irreducible representation. The index NR indicates the group operation and NCOL the column.

CARD 4 (1X,A4,5X,F3.0,3X,F4.3,3F10.7)

ID,OM,EGA,X,Y,Z

ID Name of the operation.

OM,EGA Angle of rotation in the form 2π*OM/EGA

X,Y,Z Direction cosines of the axis of rotation. The program checks the relation

$$X^2+Y^2+Z^2=1$$

CARD 5 (16I5)

LMIN,LMAX,NATOM,NFST,NLST

LMIN,LMAX Minimun and maximum value of L of the VSH's to be projected.

NATM Number of sites in the set

NFST,NLST First and last site at which are centered the VSH's to be projected

CARD 6 (2(3F10.7,I5,5X))

R(I,NS),NSITE(NS)

R x,y, and z coordinates of the site NS

NSITE Number of the site in the cluster. In the main text this is indicated by α.

CARD 7 (16I5)

NGO

If NGO=0 the program proceeds to the projection of the VSH's included in the multipolar expansion of the plane wave. If NGO$\neq$0 the program assumes that it is equal to the number of sites in the next set. In this latter case the program reads a new set of cards 5 and 6.

A2. Description of the subroutines.

In this section we describe the subroutines and functions called by the program and give a brief outline of their mode of operation.

SUBROUTINE PRMUTE

This subroutine performs the permutations induced on the sites of a given set by the operations of . According to the main text, indeed,

$$S\underline{R}_{\alpha} = \underline{R}_{\beta}$$

where S is an operation of $\mathcal{G}$ which for the present purposes is represented by a 3x3 matrix. In the present program the elements of S are expressed directly in terms of the angle of rotation, ω , and of the direction cosines of the axis, λ, μ, ν , according to the formulas

$$S_{11} = \lambda^2 + (1-\lambda^2)\cos\omega\ ,\quad S_{12} = \lambda\mu(1-\cos\omega) - \nu\sin\omega\ ,\quad S_{13} = \nu\lambda(1-\cos\omega) + \mu\sin\omega$$

$$S_{21} = \lambda\mu(1-\cos\omega) + \nu\sin\omega\ ,\quad S_{22} = \mu^2 + (1-\mu^2)\cos\omega\ ,\quad S_{23} = \mu\nu(1-\cos\omega) - \lambda\sin\omega$$

$$S_{31} = \nu\lambda(1-\cos\omega) - \mu\sin\omega\ ,\quad S_{32} = \mu\nu(1-\cos\omega) + \lambda\sin\omega\ ,\quad S_{33} = \nu^2 + (1-\nu^2)\cos\omega$$

These formulas can be proved by expressing the matrix elements of S by means of the Cayley-Klein parameters[24] as discussed below

SUBROUTINE PRJECT

This subroutine uses the projection operators of eq. (8-2), to compute the coefficients of the symmetrized combinations of magnetic and electric multipoles included in the expansion of the scattered field. Its main ingredient is the function DL described below. The coefficients of each combination are stored in the (complex) vector COF.

FUNCTION DL

This complex function computes the elements, $D^{(L)}_{M'M}(S)$, of the matrix of the operation S. Instead of using the usual form of these elements in terms of Euler angles we preferred an expression in terms of $\omega, \lambda, \mu, \nu$. Indeed, according to Hammermesh one has[25]

$$\mathcal{D}^{(L)}_{M'M}(a,b) = \sum_{\mu} \frac{[(L+M)!\,(L-M)!\,(L+M')!\,(L-M')!]^{1/2}}{(L+M-\mu)!\,\mu!\,(L-M'-\mu)!\,(M'-M+\mu)!} \times$$

$$\times\, a^{L+M-\mu}\,(a^*)^{L-M'-\mu}\, b^{\mu}\,(-b^*)^{M'-M+\mu}$$

where a and b are the Cayley-Klein parameters of the rotation, i.e. the elements of $D^{(\frac{1}{2})}$:

$$\mathcal{D}^{1/2} = \begin{pmatrix} a & b \\ -b^* & a^* \end{pmatrix}$$

To compute these quantities we recall that $D^{(L)}_{M'M}$ are the matrix elements of the rotation operator

$$\mathcal{O}_{S(\underline{\omega})} = \exp(i\,\underline{\omega}\cdot\underline{L})$$

with respect to the eigenfunctions of the angular momentum, $\underline{L}$:

$$\mathcal{D}^{(L)}_{M'M}(S) = \langle L, M' | \exp(i\,\underline{\omega}\cdot\underline{L}) | L, M\rangle = \exp i \langle L M' | \underline{\omega}\cdot\underline{L} | L, M\rangle$$

Now, it is well known that for $L=\frac{1}{2}$ one has[26)]

$$\langle \tfrac{1}{2}, M' | \underline{\omega}\cdot\underline{L} | \tfrac{1}{2}, M\rangle = \frac{\omega}{2}(\lambda\sigma_x + \mu\sigma_y + \nu\sigma_z)$$

where σ_x, σ_y and σ_z are the Pauli spin matrices. Thus

$$\lambda\sigma_x + \mu\sigma_y + \nu\sigma_z = \begin{pmatrix} \nu & \lambda - i\mu \\ \lambda + i\mu & -\nu \end{pmatrix} = \mathbb{P}$$

whence

$$\mathcal{D}^{(1/2)} = \exp\left(i\frac{\omega}{2}\mathbb{P}\right) = \sum_k \left(\frac{i\omega}{2}\right)^k \frac{1}{k!}\mathbb{P}^k =$$

$$= \sum_k \left[\left(\frac{i\omega}{2}\right)^{2k}\frac{1}{(2k)!}\mathbb{P}^{2k} + \left(\frac{i\omega}{2}\right)^{2k+1}\frac{1}{(2k+1)!}\mathbb{P}^{2k+1}\right]$$

Now

$$\mathbb{P}^{2k} = \mathbb{1} \quad , \quad \mathbb{P}^{2k+1} = \mathbb{P}$$

so that

$$\mathcal{D}^{(1/2)} = \sum_k \left[\left(\frac{i\omega}{2}\right)^{2k}\frac{1}{(2k)!}\mathbb{1} + \left(\frac{i\omega}{2}\right)^{2k+1}\frac{1}{(2k+1)!}\mathbb{P}\right] =$$

$$= \mathbb{1} \cos\frac{\omega}{2} + i\,\mathbb{P} \sin\frac{\omega}{2} =$$

$$= \begin{pmatrix} \cos\frac{\omega}{2} + i\nu \sin\frac{\omega}{2} & i(\lambda - i\mu)\sin\frac{\omega}{2} \\ i(\lambda + i\mu)\sin\frac{\omega}{2} & \cos\frac{\omega}{2} - i\nu\sin\frac{\omega}{2} \end{pmatrix}$$

whence

$$a = \cos\frac{\omega}{2} + i\nu \sin\frac{\omega}{2}$$

$$b = i(\lambda - i\mu)\sin\frac{\omega}{2}$$

The 3x3 matrix S can also be expressed in terms of a and b according to the equation

$$S = \begin{pmatrix} \frac{1}{2}(a^2 - c^2 + d^2 - b^2) & \frac{i}{2}(c^2 - a^2 + d^2 - b^2) & cd - ab \\ \frac{i}{2}(a^2 + c^2 - b^2 - d^2) & \frac{1}{2}(a^2 + c^2 + d^2 + b^2) & -i(ab + cd) \\ bd - ac & i(ac + bd & ad + bc \end{pmatrix}$$

where c=-b*, d=a*.

SUBROUTINE PRJPW

This subroutine projects all the vector spherical harmonics included in the multipolar expansion of the incident plane wave. The relevant formulas are eq. (8-2) and (8-6) and the main ingredient is still the function DL described above.

SUBROUTINE ORTHOG

This subroutine uses the Grahm-Schmidt procedure[27)] to oethogonalize to each other the combinations generated by PRJCT. A control is built in to retain only the linearly independent combinations which are also normalized to unity.

A3. Output quantities.

The output of the program CSVSH consists of three parts. The first part reproduces the names of the operations of and the corresponding parameters $\omega, \lambda, \mu, \nu$ described above. Furthermore, the permutations induced on the sites of a given set by the operations of $\mathcal{G}$ are also printed.
The second part of the output gives the coefficients of the independent combinations of magnetic and electric multipoles cenetered at the sites of the given set.
The third part gives the projection of the magnetic and of the electric multipoles included in the expansion of the incident plane wave.
In the following pages, after the references, a list of the progam is included toghether with the input data for a set of six sites at the vertices of an hexagon (structure of C_6H_6) with point group D_{6h}.

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      COMMON/ANGLES/X(48),Y(48),Z(48),UMEGA(48)
      COMMON/AY2/R(3,12)
      COMMON/REP/DN(48,3)
      COMMON/INPOUT/IR,IW,IP,II,IF
      COMMON/CC/COF(6120)
      COMMON/PARAM/MT(48,12),LMIN,LMAX,NATOM,NFST,NLST,NUPS,NINV,LTPO
      COMMON/GG/FACT(20)
      COMPLEX COF,AC,AUX
      DIMENSION NSITE(12),IDSTR(2),ID(48),DDN(12,48,3)
      DIMENSION IDREP(12),NDIM(12),AUX(100),IAUX(100)
      DATA PIG/3.141592653 5/
      LOGICAL CLEAR
      IADD4(II,JJ,KK,LL)=II+12*JJ+204*KK+2040*LL-2256
      IADPW(II,JJ,KK)=II+17*JJ+51*KK-68
      IR=1
      IP=2
      IW=3
      FACT(1)=1.
      DO 5 I=2,20
    5 FACT(I)=FACT(I-1)*FLOAT(I)
      READ(IR,1010)IDSTR,IDG,NOPS,NINV,NREP
 1010 FORMAT(3A4,3X,3I5)
      DO 10 NP=1,NREP
      READ(IR,1030)IDREP(NP),NDIM(NP)
 1030 FORMAT(15X,A4,5X,I2)
 1000 FORMAT(16I5)
      NNDIM=NDIM(NP)
      IDR=IDREP(NP)
      DO 10 NCOL=1,NNDIM
      READ(IR,1040)(DDN(NP,NR,NCOL),NR=1,NOPS)
 1040 FORMAT(4F10.7)
   10 CONTINUE
      DO 20 NR=1,NOPS
      READ(IR,1020)ID(NR),OM,EGA,X(NR),Y(NR),Z(NR)
 1020 FORMAT (1X,A4,5X,F3.0,3X,F4.3,3F10.7)
      UMEGA(NR)=OM/EGA
 5020 FORMAT(1H ,13X,A4,2X,4F15.7)
   20 UMEGA(NR)=UMEGA(NR)*PIG
      READ(IR,1000)LMIN,LMAX,NATOM,NFST,NLST
      IF(NFST.EQ.0)NFST=1
      IF(NLST.EQ.0)NLST=NATOM
      WRITE(IW,5000)LMIN,LMAX,IDSTR,IDG
 5000 FORMAT(1H1,/////,20X,'SYMMETRIZED COMBINATIONS OF MULTIPOLES FROM
     *L=',I2,'  TO L=',I2,/,26X,'FOR THE STRUCTURE OF '2A4,' WITH GROUP
     *',A4,/////)
      WRITE(IW,5010).
 5010 FORMAT(1H ,9X,'OPERATION',10X,'X',14X,'Y',14X,'Z',10X,'OMEGA/PIG')
      WRITE(IW,5020)(ID(NR),X(NR),Y(NR),Z(NR),UMEGA(NR),NR=1,NOPS)
   25 READ(IR,1025)((R(I,NS),I=1,3),NSITE(NS),NS=1,NATOM)
 1025 FORMAT(2(3F10.7,I5,5X))
      IF(NATOM.EQ.1)GO TO 28
      WRITE(IW,5030)
 5030 FORMAT(1H1,10X,'OPERATION',37X,'PERMUTATION')
      DO 27 NR=1,NOPS
      CALL PRMUTE(NR)
   27 WRITE(IW,5040)ID(NR),(MT(NR,NS),NS=1,NATOM)
 5040 FORMAT(1H ,13X,A4,2X,12I7)
   28 DO 110 NP=1,NREP
      WRITE(IW,5005)
 5005 FORMAT(1H1)
      NNDIM=NDIM(NP)
      IDR=IDREP(NP)
      WRITE(IW,5035)IDR,NNDIM
 5035 FORMAT(1H ,10X,'REPRESENTATION ',A4,' OF DIMENSION',I3)
      DO 30 NCOL=1,NNDIM
      DO 29 NR=1,NOPS
   29 DN(NR,NCOL)=DDN(NP,NR,NCOL)
      WRITE(IW,5050)NCOL
 5050 FORMAT(1H ,//,15X,'ROW 1',5X,'COLUMN'I3)
   30 WRITE(IW,5060)(DN(NR,NCOL),NR=1,NOPS)
 5060 FORMAT(1H ,8F14.8)
      LMNPO=LMIN+1
      LMXPO=LMAX+1
      DO 110 LPO=LMNPO,LMXPO
      L=LPO-1
      LTPO=2*L+1
      DO 110 IME=1,2
      NBAS=1
      IPAR=IME-1
      IF(IPAR.NE.0)GO TO 32
      WRITE(IW,5065)
 5065 FORMAT(1H ,///,20X,'MAGNETIC MULTIPOLES',/)
      GO TO 33
```

```
      30 WRITE(IW,5030)
    5030 FORMAT(1H ,///,20X,'ELECTRIC MULTIPOLES'/)
      35 DO 40 NS=NFST,NLST
         DO 40 IM=1,LTPO
         CALL PROJECT(LPO,NS,IM,NBAS,1,IPAR,(1.,0.),.TRUE.)
      40 CALL ORTHOG(NBAS)
         NBAS=NBAS-1
         WRITE(IW,5070)NNDIM,NBAS
    5070 FORMAT(1H ,//,60X,'NDIM=',I4,27X,'NBAS=',I4)
         IF(NBAS.EQ.0)GO TO 100
         IF(NNDIM.EQ.1)GO TO 70
         DO 60 NCOL=2,NNDIM
         DO 60 NB=1,NBAS
         CLEAR=.TRUE.
         DO 50 NS=1,NATOM
         DO 50 IM=1,LTPO
         IADDR=IADDR(NS,IM,NB,1)
         AC=COF(IADDR)
         IF(CABS(AC).LT.1.E-4)GO TO 50
         CALL PROJECT(LPO,NS,IM,NB,NCOL,IPAR,AC,CLEAR)
         CLEAR=.FALSE.
      50 CONTINUE
         FAC=FLOAT(NNDIM)/NOPS
         DO 60 NS=1,NATOM
         DO 60 IM=1,LTPO
         IADDR=IADDR(NS,IM,NB,NCOL)
         COF(IADDR)=COF(IADDR)*FAC
      60 CONTINUE
      70 DO 90 NCOL=1,NNDIM
         DO 90 NB=1,NBAS
         IF(NNDIM.NE.1)WRITE(IW,5080)L,NCOL
         IF(NNDIM.EQ.1)WRITE(IW,5090)L
    5080 FORMAT(1H ,/,50X,'L=',I3,' COLUMN=',I3,/)
    5090 FORMAT(1H ,60X,'L='I3,/)
         NCOUNT=0
         NMS=0
         DO 90 IM=1,LTPO
         SUM=0.0
         DO 80 NS=1,NATOM
         IADDR=IADDR(NS,IM,NB,NCOL)
         IF(CABS(COF(IADDR)).GT.1.E-4)GO TO 75
         COF(IADDR)=(0.0,0.0)
         GO TO 80
      75 NCOUNT=NCOUNT+1
         AUX(NCOUNT)=COF(IADDR)
         IAUX(NCOUNT)=NSITE(NS)
         SUM=SUM+CABS(COF(IADDR))
      80 CONTINUE
         IF(SUM.LT.1.E-4)GO TO 90
         IADDR=IADDR(0,IM,NB,NCOL)
         M=IM-LPO
         WRITE(IW,5100) M,(COF(IADDR+NS),NSITE(NS),NS=1,NATOM)
         WRITE(12,7000)(AUX(N),IAUX(N),N=1,NCOUNT)
    7000 FORMAT(2(2E16.8,I3))
         NMS=NMS+NATOM
      90 CONTINUE
    5100 FORMAT(1H ,2X,'M=',I3,4(5X,'(',F8.5,',',F8.5,')',I3)/,8X,4(5X,'(',
        *F8.5,',',F8.5,')',I3))
         GO TO 110
     100 WRITE(IW,5110)L
     110 CONTINUE
         READ(IR,1000)NSO
         IF(NSO.EQ.0)GO TO 120
         NATOM=NSO
         GO TO 25
     120 WRITE(IW,5120)LMIN,LMAX
    5120 FORMAT(1H1,20X,'SYMMETRY DECOMPOSITION OF THE INCIDENT PLANE',/,
        *20X,'WAVE FROM L=',I2,' TO L=',I2,///)
         DO 160 NP=1,NREP
         NNDIM=NDIM(NP)
         IOR=IORREP(NP)
         WRITE(IW,5135)IOR,NNDIM
    5135 FORMAT(1H1,10X,'REPRESENTATION ',A4,' OF DIMENSION',I3)
         DO 160 NCOL=1,NNDIM
         DO 130 NR=1,NOPS
     130 DN(NR,NCOL)=DD(NP,NR,NCOL)
         DO 160 LPO=LMNPO,LMXPO
         DO 160 IME=1,2
         IPAR=IME-1
         IF(IPAR.NE.0)GO TO 140
         WRITE(IW,5165)
         GO TO 150
     140 WRITE(IW,5095)
```

```
  150 CALL PRJPW(LPO,NCOL,WAR,NNDIM)
  160 CONTINUE
      STOP
 5110 FORMAT(1H ,20X,'NO BASIS FOUND FOR L=',I3)
      END
```

```
      SUBROUTINE [illegible](IPG,NSITE,IM,NBAS,NCOL,IPAR,CONST,CLEAR)
      COMMON/[illegible]/IW
      COMMON/KEP/[illegible]
      COMMON/[illegible]/[illegible]
      COMMON/[illegible]/AT([illegible]),LMIN,LMAX,NATOM,NFST,NLST,NOPS,NINV,LIPG
      COMPLEX [illegible],CONST,CC,COL
      [illegible]
      I[illegible](II,JJ,KK,LL)=II+12*JJ+204*KK+2040*LL-2256
      IF([illegible]) GO TO 100
      IF([illegible]) GO TO 100
      IF([illegible].CLEAR) GO TO 20
      DO 10 [illegible]=1,[illegible]M
      DO 10 [illegible]=1,LIPG
      IADDR=INDEX([illegible],MM,NBAS,NCOL)
   10 COF(IADDR)=(0.0,0.0)
   20 M=IM-LPG
      [illegible]=[illegible]-1
      DO 30 IMP=1,LIPG
      [illegible]=IMP-[illegible]
      [illegible]=1,NOPS
      COL=[illegible](MP,M,[illegible])
      CC=C*[illegible]
      IF([illegible]) COL=-COL
      IF(MT(NR,NSITE)[illegible]) GO TO 100
      [illegible]=MT(NR,NSITE)
      IADDR=INDEX([illegible],IMP,NBAS,NCOL)
   30 COF(IADDR)=COF(IADDR)+[illegible](NR,NCOL)*COL*CONST
      RETURN
  100 WRITE(IW,110)[illegible],NSITE,MT(NR,NSITE),MP,NBAS,NCOL,M
  110 FORMAT(7I5,' STOP IN PROJECT')
      RETURN
      END
```

```
      SUBROUTINE ORTHOG(NBAS)
      COMMON/CC/COF(6120)
      COMMON/PARAM/MT(48,12),LMIN,LMAX,NATOM,NFST,NLST,NOPS,NINV,LTPO
      COMPLEX COF,PROD
      IADD4(II,JJ,KK,LL)=II+12*JJ+204*KK+2040*LL-2256
      IF(NBAS.EQ.1)GO TO 40
C               ORTHOGONALIZATION
      NN1=NBAS-1
      DO 30 N=1,NN1
      PROD=(0.0,0.0)
      DO 10 IM=1,LTPO
      DO 10 NS=1,NATOM
      IADDR=IADD4(NS,IM,NBAS,1)
      JADDR=IADD4(NS,IM,N,1)
   10 PROD=PROD+COF(IADDR)*CONJG(COF(JADDR))
      DO 20 IM=1,LTPO
      DO 20 NS=1,NATOM
      IADDR=IADD4(NS,IM,NBAS,1)
      JADDR=IADD4(NS,IM,N,1)
   20 COF(IADDR)=COF(IADDR)-PROD*COF(JADDR)
   30 CONTINUE
C               NORMALIZATION
   40 PD=0.0
      DO 50 IM=1,LTPO
      DO 50 NS=1,NATOM
      IADDR=IADD4(NS,IM,NBAS,1)
   50 PD=PD+COF(IADDR)*CONJG(COF(IADDR))
      IF(PD.LT.1.E-4)RETURN
      PD=SQRT(PD)
      DO 60 IM=1,LTPO
      DO 60 NS=1,NATOM
      IADDR=IADD4(NS,IM,NBAS,1)
   60 COF(IADDR)=COF(IADDR)/PD
      NBAS=NBAS+1
      RETURN
      END
```

```
      SUBROUTINE PRMOTE(NR)
      COMMON/INPUT/IR,IW
      COMMON/ANGLES/X(48),Y(48),Z(48),OMEGA(48)
      COMMON/XYZ/R(3,12)
      COMMON/PARAM/MT(48,12),LMIN,LMAX,NATOM,NFST,NLST,NOPS,NINV
      DIMENSION A(3,3),S(3)
      XX=X(NR)
      YY=Y(NR)
      ZZ=Z(NR)
      RHO=SQRT(XX*XX+YY*YY+ZZ*ZZ)
      IF(RHO.LT.1.E-04) GO TO 5
      XX=XX/RHO
      YY=YY/RHO
      ZZ=ZZ/RHO
    5 RA=OMEGA(NR)
      X2=XX*XX
      Y2=YY*YY
      Z2=ZZ*ZZ
      CRA=COS(RA)
      A(1,1)=X2+(1.-X2)*CRA
      A(2,2)=Y2+(1.-Y2)*CRA
      A(3,3)=Z2+(1.-Z2)*CRA
      SRA=SIN(RA)
      CRA=1.-CRA
      E=XX*YY*CRA
      F=ZZ*SRA
      A(1,2)=E-F
      A(2,1)=E+F
      E=XX*ZZ*CRA
      F=YY*SRA
      A(1,3)=E+F
      A(3,1)=E-F
      E=YY*ZZ*CRA
      F=XX*SRA
      A(2,3)=E-F
      A(3,2)=E+F
      DO 40 M=1,NATOM
      DO 10 I=1,3
      S(I)=0.0
      DO 10 J=1,3
   10 S(I)=S(I)+A(I,J)*R(J,M)
      IF(NR.LE.NINV)GO TO 20
      S(1)=-S(1)
      S(2)=-S(2)
      S(3)=-S(3)
   20 DO 30 MP=1,NATOM
      RS=ABS(R(1,MP)-S(1))+ABS(R(2,MP)-S(2))+ABS(R(3,MP)-S(3))
      IF(RS.LT.1.E-2)GO TO 40
   30 CONTINUE
      WRITE(IW,50)NR,M,S(1),S(2),S(3)
      STOP
   40 MT(NR,M)=MP
      RETURN
   50 FORMAT(20X,'STOP IN PRMOTE',2I5,3F14.7)
      END
```

```
      COMPLEX FUNCTION DL(L,MP,M,NK)
      COMMON/ANGLES/ALPHA(48),BETA(48),GAMMA(48),OMEGA(48)
      COMMON/GG/FACT(20)
      COMPLEX B,D,G
      DIMENSION NF(4)
      EQUIVALENCE (N1,NF(1)),(N2,NF(2)),(N3,NF(3)),(N4,NF(4))
      IF(L.NE.0)GO TO 10
      DL=(1.0,0.0)
      RETURN
   10 DL=(0.0,0.0)
      X=ALPHA(NK)
      Y=BETA(NK)
      Z=GAMMA(NK)
      KA=OMEGA(NK)/2.
      IF(ABS(KA).LT.1.E-04)GO TO 70
      RHO=X*X+Y*Y
      ZZ=Z*Z
      N1=L+M
      N2=L-M
      N3=L+MP
      N4=L-MP
      F=1.0
      DO 20 N=1,4
      NN=NF(N)
      IF(NN.EQ.0)GO TO 20
      F=F*FACT(NN)
   20 CONTINUE
      F=SQRT(F)
      SKA=SIN(KA)
      CKA=COS(KA)
      SKAS=SKA*SKA
      CKAS=CKA*CKA
      IF(CKAS.LE.1.E-4.AND.ZZ.LE.1.E-4) GO TO 50
      IF(RHO.LE.1.E-4.OR.SKAS.LE.1.E-4)GO TO 60
      A=CKAS+ZZ*SKAS
      B=CMPLX(CKA,+Z*SKA)
      C=RHO*SKAS
      D=CMPLX(Y,-X)*SKA
      S=C/A
      G=F*A**(L-MP)*B**(M+MP)*D**(MP-M)
      KMIN=MAX0(M-MP,0)+1
      KMAX=MIN0(L+M,L-MP)+1
      SUM=0.0
      DO 40 KK=KMIN,KMAX
      K=KK-1
      N1=L+M-K
      N2=L-MP-K
      N3=K
      N4=MP-M+K
      TERM=S**K
      DO 30 N=1,4
      NN=NF(N)
      IF(NN.EQ.0)GO TO 30
      TERM=TERM/FACT(NN)
   30 CONTINUE
      IF(MOD(MP-M+K,2).NE.0)TERM=-TERM
   40 SUM=SUM+TERM
      DL=G*SUM
      RETURN
   50 IF(MP+M.NE.0)RETURN
      DL=CMPLX(Y,-X)**(2*MP)
      IF(MOD(L+MP,2).NE.0)DL=-DL
      RETURN
   60 IF(MP.NE.M)RETURN
      DL=CMPLX(CKA,Z*SKA)**(2*MP)
      RETURN
   70 IF(MP.NE.M)RETURN
      DL=(1.0,0.0)
      RETURN
      END
```

```
      SUBROUTINE PROJP(LPO,NCOL,IPAR,NNOIM)
      COMMON/INPOUT/IR,IW,IP,IT,II
      COMMON/REP/ON(48,3)
      COMMON/PARAM/MT(48,12),LMIN,LMAX,NATOM,NFST,NLST,NOPS,NINV,LTPO
      DIMENSION CFPW(17,17),AUX(17),IAUX(17)
      COMPLEX CFPW,COL,DL,AUX
      DO 10 I=1,17
      DO 10 J=1,17
   10 CFPW(I,J)=(0.0,0.0)
      FAC=FLOAT(NNOIM)/NOPS
      L=LPO-1
      LL=IPAR+L
      DO 30 IM=1,LTPO
      M=IM-LPO
      DO 30 IMP=1,LTPO
      MP=IMP-LPO
      DO 30 NR=1,NOPS
      COL=DL(L,MP,M,NR)
      IF(NR.GT.NINV.AND.MOD(LL,2).NE.0)COL=-COL
   30 CFPW(IM,IMP)=CFPW(IM,IMP)+ON(NR,NCOL)*COL*FAC
      IF(NNOIM.NE.1)WRITE(IW,5090)L
      IF(NNOIM.EQ.1)WRITE(IW,5080)L,NCOL
      DO 45 IM=1,LTPO
      M=IM-LPO
      WRITE(IW,510)M
  510 FORMAT(1H ,2X,'M=',I2)
      DO 40 IMP=1,LTPO
      MP=IMP-LPO
      IAUX(IMP)=MP
   40 AUX(IMP)=CFPW(IM,IMP)
   45 WRITE(IW,500)(IAUX(IMP),AUX(IMP),IMP=1,LTPO)
  500 FORMAT(1H ,4(I2,2X,2F8.5))
 5080 FORMAT(1H ,/,50X,'L=',I3,' COLUMN=',I3,/)
 5090 FORMAT(1H ,60X,'L='I3,/)
      RETURN
      END
```

```
[illegible]                  24    12    12
                    A1G          1
 1.0        1.0         1.0         1.0         1.0         1.0         1.0         1.0
 1.0        1.0         1.0         1.0         1.0         1.0         1.0         1.0
 1.0        1.0         1.0         1.0         1.0         1.0         1.0         1.0
                    A2G          1
 1.0        1.0         1.0         1.0         1.0         1.0        -1.0        -1.0
-1.0       -1.0        -1.0        -1.0         1.0         1.0         1.0         1.0
 1.0        1.0        -1.0        -1.0        -1.0        -1.0        -1.0        -1.0
                    B1G          1
 1.0       -1.0        -1.0         1.0         1.0        -1.0         1.0         1.0
 1.0       -1.0        -1.0        -1.0         1.0        -1.0        -1.0         1.0
 1.0       -1.0         1.0         1.0         1.0        -1.0        -1.0        -1.0
                    B2G          1
 1.0       -1.0        -1.0         1.0         1.0        -1.0        -1.0        -1.0
-1.0        1.0         1.0         1.0         1.0        -1.0        -1.0         1.0
 1.0       -1.0        -1.0        -1.0        -1.0         1.0         1.0         1.0
                    E1G          2
 1.0        0.5         0.5        -0.5        -0.5        -1.0         1.0        -0.5
-0.5        0.5        -1.0         0.5         1.0         0.5         0.5        -0.5
-0.5       -1.0         1.0        -0.5        -0.5         0.5        -1.0         0.5
 0.0        0.8660254-0.8660254 0.8660254-0.8660254 0.0         0.0         0.8660254
-0.8660254  0.8660254 0.0        -0.8660254 0.0         0.8660254-0.8660254 0.8660254
-0.8660254  0.0       0.0         0.8660254-0.8660254 0.8660254 0.0        -0.8660254
                    E2G          2
 1.0       -0.5        -0.5        -0.5        -0.5         1.0        -1.0         0.5
 0.5        0.5        -1.0         0.5         1.0        -0.5        -0.5        -0.5
-0.5        1.0        -1.0         0.5         0.5         0.5        -1.0         0.5
 0.0       -0.8660254 0.8660254 0.8660254-0.8660254 0.0         0.0        -0.8660254
 0.8660254  0.8660254 0.0        -0.8660254 0.0        -0.8660254 0.8660254 0.8660254
-0.8660254  0.0       0.0        -0.8660254 0.8660254 0.8660254 0.0        -0.8660254
                    A1U          1
 1.0        1.0         1.0         1.0         1.0         1.0         1.0         1.0
 1.0        1.0         1.0         1.0        -1.0        -1.0        -1.0        -1.0
-1.0       -1.0        -1.0        -1.0        -1.0        -1.0        -1.0        -1.0
                    A2U          1
 1.0        1.0         1.0         1.0         1.0         1.0        -1.0        -1.0
-1.0       -1.0        -1.0        -1.0        -1.0        -1.0        -1.0        -1.0
-1.0       -1.0         1.0         1.0         1.0         1.0         1.0         1.0
                    B1U          1
 1.0       -1.0        -1.0         1.0         1.0        -1.0         1.0         1.0
 1.0       -1.0        -1.0        -1.0        -1.0         1.0         1.0        -1.0
-1.0        1.0        -1.0        -1.0        -1.0         1.0         1.0         1.0
                    B2U          1
 1.0       -1.0        -1.0         1.0         1.0        -1.0        -1.0        -1.0
-1.0        1.0         1.0         1.0        -1.0         1.0         1.0        -1.0
-1.0        1.0         1.0         1.0         1.0        -1.0        -1.0        -1.0
                    E1U          2
 1.0        0.5         0.5        -0.5        -0.5        -1.0         1.0        -0.5
-0.5        0.5        -1.0         0.5        -1.0        -0.5        -0.5         0.5
 0.5        1.0        -1.0         0.5         0.5        -0.5         1.0        -0.5
 0.0        0.8660254-0.8660254 0.8660254-0.8660254 0.0         0.0         0.8660254
-0.8660254  0.8660254 0.0        -0.8660254 0.0        -0.8660254 0.8660254-0.8660254
 0.8660254  0.0       0.0        -0.8660254 0.8660254-0.8660254 0.0         0.8660254
                    E2U          2
 1.0       -0.5        -0.5        -0.5        -0.5         1.0        -1.0         0.5
 0.5        0.5        -1.0         0.5        -1.0         0.5         0.5         0.5
 0.5       -1.0         1.0        -0.5        -0.5        -0.5         1.0        -0.5
 0.0       -0.8660254 0.8660254 0.8660254-0.8660254 0.0         0.0        -0.8660254
 0.8660254  0.8660254 0.0        -0.8660254 0.0         0.8660254-0.8660254-0.8660254
 0.8660254  0.0       0.0         0.8660254-0.8660254-0.8660254 0.0         0.8660254
E          0PI/1      0.0         0.0         0.0
C6         2PI/6      0.0         0.0         1.0
C6        -2PI/6      0.0         0.0         1.0
C3         2PI/3      0.0         0.0         1.0
C3        -2PI/3      0.0         0.0         1.0
C2         2PI/2      0.0         0.0         1.0
C2         2PI/2      1.0         0.0         0.0
C2         2PI/2      0.5         0.8660254   0.0
C2         2PI/2     -0.5         0.8660254   0.0
C2         2PI/2      0.8660254   0.5         0.0
C2         2PI/2      0.0         1.0         0.0
C2         2PI/2     -0.8660254   0.5         0.0
E*I        0PI/1      0.0         0.0         0.0
C6*I       2PI/6      0.0         0.0         1.0
C6*I      -2PI/6      0.0         0.0         1.0
C3*I       2PI/3      0.0         0.0         1.0
C3*I      -2PI/3      0.0         0.0         1.0
C2*I       2PI/2      0.0         0.0         1.0
C2*I       2PI/2      1.0         0.0         0.0
C2*I       2PI/2      0.5         0.8660254   0.0
```

```
00032    C2*1      2PI/2    -0.5        0.8660254   0.0
00033    C2*1      2PI/2    0.8660254   0.5         0.0
00034    C2*1      2PI/2    0.0         1.0         0.0
00035    C2*1      2PI/2    -0.8660254  0.5         0.0
00036       1     1     6     1     1
00037    1.0       0.0          0.0          2    0.5     0.8660254 0.0          4
00038    -0.5      0.8660254    0.0          5    -1.0    0.0          0.0       6
00039    -0.5      -0.8660254   0.0          7    0.5     -0.8660254 0.0          8
00040
```

DATE
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